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Přesné výpočty energií elektronových hladin atomů

Dizertační práce

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Obsah

Kapitola 1

Úvod

1.1 Motivace

Struktura atomových spekter je v zásadě popsána nerelativistickou kvantovou mechanikou a Coulombovou interakcí. Jemná struktura atomových spekter je dána interakcemi, které jsou vzhledem k elektrostatické interakci poměrně slabé. Jsou to zejména relativistické efekty (magnetické efekty, závislost hmotnosti na rychlosti), radiační korekce popsané kvantovou elektrodynamikou a efekty slabých interakcí.

Experimentální zjištění vlnové délky spektrálních čar nabylo takové přesnosti, že je možno detekovat efekty slabých interakcí [6]. Pozorování těchto efektů je důležité při ověřování platnosti tzv. "Standardního modelu" a dále umožňuje stanovit meze pro hmotnosti intermediálních bozonů, které byly předpovězeny rozšířeními standardního modelu.

Vzhledem k tomu, že tyto efekty jsou velice malé, je potřeba umět počítat základní strukturu spekter s vysokou přesností. Aby se dosáhlo takové přesnosti, je potřeba provádět výpočty značného rozsahu. V těchto výpočtech je numerická stabilita zásadní problém.

Numerická přesnost je zásadní problém při všech vědecko-technických výpočtech, nejen v případě výpočtu spekter atomů. Problému numerické stability proto byla a je věnována značná pozornost. V této souvislosti je třeba upozornit na práce [7] a [4], ve kterých bylo ukázáno jak velmi efektivně pracovat s čísly podstatně vyšší numerické přesnosti, než je strojová přesnost. Například jak provádět celé výpočty v 128 a 64 místné aritmetice na strojích s 32 místnou aritmetikou. Je však zřejmé, že se zvyšujícím se počtem platných míst ve výpočtech rostou nároky na množství strojové paměti a času. I přesto, že v poslední době se rychle zlepšují technické parametry výpočetní techniky, je žádoucí vyvíjet takové algoritmy, které vyžadují co nejmenší numerickou přesnost a mají tedy menší technologické náklady a umožní provádět výpočty většího rozsahu. Vývoj těchto metod a algoritmů pro výpočty atomových spekter je předmětem této práce.

1.2 Vymezení problému

Nejpřesnější přibližná metoda výpočtu energií elektronových hladin bez použití relativistických korekcí je metoda konfigurační interakce (CI). Ta je založená na rozvoji přesné mnoha-elektronové vlnové funkce do antisymetrizovaných součinů jednoelektronových spinorbitalů (Slaterových determinantů). Přesnost může být jednoduše zvětšována zvyšováním počtu jednoelektronových spinorbitalů (a tedy i Slaterových determinantů). Výpočet maticových elementů Coulombovské interakce mezi dvěma spinorbitaly lokalizovanými na stejném atomu vede k výpočtu dvouelektronových integrálů typu

$$\int d^3r_1 \int d^3r_2 R_{n1_i,l1_i}(r_1\xi_{1i}) Y_{l1_i,m1_i}(\vec{n}_1) R_{n2_i,l2_i}(r_2\xi_{2i}) Y_{l2_i,m2_i}(\vec{n}_2) \times \\ \times r_{12}^{-1} R_{n1_j,l1_j}(r_1\xi_{1j}) Y_{l1_j,m1_j}(\vec{n}_1) R_{n2_j,l2_j}(r_2\xi_{2j}) Y_{l2_j,m2_j}(\vec{n}_2), \tag{1.1}$$

kde $Y_{l,m}(\vec{n})$ značí kulové funkce [1] a $R_{n,l}(\xi r)$ jsou radiální funkce [2] (Laguerrovy polynomy).

Tvar jednoelektronových spinorbitalů může být v principu libovolný (samozřejmě s podmínkou, že spinorbitaly musí tvořit bázi), nicméně je známo, že použití Sturmovy [3] báze s funkcemi

$$R_{n,l}(r) = 2\sqrt{\frac{(n-l-1)!}{(n+l)!}} e^{-r} (2r)^l L_{n-l-1}^{2l+1}(2r) \; , \tag{1.2}$$

kde $L_{n-1}^1(2r)$ jsou zobecněné Laguerrovy polynomy vede k rychlé konvergenci CI metody.

Použitím explicitního tvaru Laguerrových polynomů je možno zapsat radiální funkce $R_n(r)$ jako lineární kombinace Slaterových funkcí, úměrných exponenciále a mocnině r^q

$$R_n(r) = 2 \sum_{q=0}^{n-l-1} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \times$$

---

[1] $Y_{l,m}(\vec{n}) = Ne^{im\varphi} P_l^m cos(\theta)$, kde $P_l^m cos(\theta)$ jsou přidružené Legendrovy funkce.

[2] ξ_{1i}, ξ_{2i}, ξ_{1j} a ξ_{2j} jsou příslušné stínící konstanty. $\vec{n_1}$ a $\vec{n_2}$ jsou jednotkové vektory v příslušném směru.

[3] Takzvané Sturmovy funkce dostaneme obecně jako řešení rovnice $(D+\beta_n V_0 - E)\psi_n = 0$, kde D je diferenciální operátor. Místo vlastního problému hledáme takové β_n pro které je splněna tato rovnice při daném E. Hledáme tedy $E(\beta_n)$. V případě Schrödingerovy rovnice s Coulombovým potenciálem β_n závisí pouze na hlavním kvantovém čísle n a nezávisí na kvantových číslech l a m. Sturmova báze je spočetná a úplná.

$$\times \frac{(n+l)!2^{q+l}}{(n-l-1-q)!q!(2l+1+q)!} (-1)^q e^{-r} r^{q+l} \,. \tag{1.3}$$

Dosazením do (1.2) integrály dostanou tvar lineární kombinace integrálů

$$\int_0^\infty dr_1 e^{-2r_1} r_1^a \int_0^{r_1} dr_2 e^{-2r_2} r_2^b \,, \tag{1.4}$$

které jsou snadno spočitatelné. Dá se snadno ověřit, že výpočet koeficientů lineární kombinace je však s použitím aritmetiky s konečnou přesností značně numericky nestabilní.

Bázové funkce jsou ortogonální, což vede k tomu, že funkce odpovídající vysoce excitovaným stavům mají mnoho uzlů (mění znaménko). Důsledkem toho je, že se při výpočtu maticových elementů Coulombovské interakce mezi dvěma vlnovými funkcemi, které jsou sestavené v této bázi, vytváří numerické nestability. V případě, že se místo ortogonálních funkcí použijí neortogonální funkce (které tvoří úplnou bázi), se problém přesune do procesu diagonalizace.

Numericky stabilní výpočet uvedených integrálů se dá provést s využitím faktu, že radiální funkce splňují určité rekurentní relace. Tyto relace se dají použít k odvození rekurentních relací mezi integrály z těchto funkcí. Tímto způsobem je výpočet integrálů (elegantně) převeden na řešení diferenčních rovnic a numerické nestability se pak dají přiměřeně snadno obejít.

Takovouto metodu se podařilo naší skupině vyvinout, naprogramovat a otestovat na příkladu atomu Helia. V dalším textu budou popsány ideje, na kterých je tato metoda postavena, její popis a výsledky numerických testů na případu atomu He a jejich porovnání s experimentálními daty.

Kapitola 2

Řešení problému

2.1 Spektrum generující algebry

Výpočet atomových integrálů vychází z algebraického řešení Schrödingerovy rovnice, založeném na výsledcích teorie kompaktních grup a jejich Lieových algeber [1]. Dá se ukázat, že když vyjdeme ze základních komutačních relací pro kanonicky sdružené proměnné, například souřadnice a impulsu, můžeme sestrojit generátory so(2,1) algebry [3], [2]. Tento postup je aplikovatelný na libovolný pár kanonicky sdružených souřadnic a k nim příslušných momentů. Uvažujme operátor $\hat{R}$ v N-dimenzionálním eukleidovském prostoru,

$$\hat{R} \equiv R = \left(\sum_{j=1}^{N} X_j^2 \right)^{\frac{1}{2}} , \tag{2.1}$$

kde X_j jsou jednotlivé souřadnice a k němu sdružený moment $\hat{P}_R$ (pro N=3)

$$\hat{P}_R \equiv -iR^{-M} \frac{\partial}{\partial R} R^M = -i \left(\frac{\partial}{\partial R} + f(R) \right) , \tag{2.2}$$

kde $f(R) = \frac{M}{R}$ a $M = \frac{1}{2}(N-1)$; (zde je N obecné). Komutační relace (zde používáme $\hbar = 1$)

$$[\hat{R}, \hat{P}_R] = i \tag{2.3}$$

---

[1] Lineární prostor, na němž je definována další bilineární operace [A,B], zvaná komutátor, splňující vztahy $[A,B] = -[B,A]$ a $[A,[B,C]] + [B,[C,A]] + [C,[A,B]] = 0$ se nazývá Lieova algebra.

platí pro libovolnou funkci $f(r)$. Z uvedené komutační relace pak plyne

$$[\hat{R}^n, \hat{P}_R] = \sum_{j=0}^{n-1} \hat{R}^j [\hat{R}, \hat{P}_R] \hat{R}^{n-1-j} = in\hat{R}^{n-1} \tag{2.4}$$

a analogicky

$$[\hat{R}, \hat{P}_R^n] = in\hat{P}_R^{n-1} \ . \tag{2.5}$$

Vynásobením rovnice (2.4) $\hat{R}$ a po následné úpravě dostaneme

$$[\hat{R}^n, \hat{R}\hat{P}_R] = in\hat{R}^n \ , \tag{2.6}$$

přičemž bylo použito vztahu

$$F(\hat{A})[G(\hat{A}), \hat{B}] = [G(\hat{A}), F(\hat{A})\hat{B}] \ , \tag{2.7}$$

kde $F(\hat{A})$ a $G(\hat{A})$ jsou libovolné funkce operátoru $\hat{A}$. Úpravami výše uvedených rovnic se dá ukázat, že operátory $\hat{R}\hat{P}_R^m$ a $\hat{R}\hat{P}_R^n, (m \neq n)$ generují neabelovskou dvou-dimenzionální Lieovu algebru, když $(n + m - 1) = m$ nebo $(n + m - 1) = n$ nebo $m = 1$ nebo $n = 1$. Dá se ukázat, že operátory $\hat{R}$, $\hat{R}\hat{P}_R$ a $\hat{R}\hat{P}_R^2$ generují třídimenzionální Lieovu algebru definovanou komutačními relacemi (viz [14])

$$[\hat{R}\hat{P}_R, \hat{R}] = -i\hat{R} \tag{2.8}$$

$$[\hat{R}\hat{P}_R, \hat{R}\hat{P}_R^2] = i\hat{R}\hat{P}_R^2 \tag{2.9}$$

$$[\hat{R}, \hat{R}\hat{P}_R^2] = 2i\hat{R}\hat{P}_R \ . \tag{2.10}$$

Tyto relace je možno zobecnit na tvar

$$[\hat{R}^n, \hat{R}\hat{P}_R] = in\hat{R}^n \tag{2.11}$$

$$[\hat{R}\hat{P}_R, \hat{R}^{2-n}\hat{P}_R^2] = in\hat{R}^{2-n}\hat{P}_R^2 \tag{2.12}$$

$$[\hat{R}^n, \hat{R}^{2-n}\hat{P}_R^2] = 2in\left\{\hat{R}\hat{P}_R - \frac{i}{2}(n-1)\hat{I}\right\} \ . \tag{2.13}$$

Zavedením vhodných substitucí $\hat{V}_1$, $\hat{V}_2$, $\hat{V}_3$

$$\hat{V}_1 = \hat{R}^n \tag{2.14}$$

$$\hat{V}_2 = n^{-1}\left[\hat{R}\hat{P}_R - \frac{i}{2}(n-1)\hat{I}\right] \tag{2.15}$$

$$\hat{V}_3 = n^{-2}\hat{R}^{2-n}\hat{P}_R^2 \tag{2.16}$$

($\hat{V}_1$, $\hat{V}_2$, $\hat{V}_3$ jsou generátory příslušné Lieovy algebry) lze tyto komutační relace převést do tvaru

$$[\hat{V}_1, \hat{V}_2] = i\hat{V}_1 \tag{2.17}$$

$$[\hat{V}_2, \hat{V}_3] = i\hat{V}_3 \tag{2.18}$$

$$[\hat{V}_1, \hat{V}_3] = 2i\hat{V}_2 \ . \tag{2.19}$$

Z uvedených operátorů $\hat{V}$ se dá sestavit báze analogická bázi operátoru momentu hybnosti. Operátor $\hat{V}_2$ je jeden z generátorů. Hledanou transformaci obdržíme sčítáním a odečítáním relací (2.17) a (2.18)

$$[\hat{V}_3 \pm \hat{V}_1, \hat{V}_2] = -i(\hat{V}_3 \pm \hat{V}_1) \ . \tag{2.20}$$

Pro lineární kombinace V_1 a V_3 dostaneme z (2.19) tuto komutační relaci

$$[\hat{V}_3 + \hat{V}_1, \hat{V}_3 - \hat{V}_1] = [\hat{V}_1, \hat{V}_3] - [\hat{V}_3, \hat{V}_1] = 4i\hat{V}_2 \ . \tag{2.21}$$

Odtud je vidět, že můžeme definovat operátory $\hat{T}_i$

$$\hat{T}_1 = \frac{1}{2}(\hat{V}_3 - \hat{V}_1) \ , \tag{2.22}$$

$$\hat{T}_2 = \hat{V}_2 \ , \tag{2.23}$$

$$\hat{T}_3 = \frac{1}{2}(\hat{V}_3 + \hat{V}_1) \ , \tag{2.24}$$

takže obdržíme relace

$$[T_1, T_2] = -iT_3 \ , \tag{2.25}$$

$$[T_2, T_3] = iT_1 \ , \tag{2.26}$$

$$[T_3, T_1] = iT_2 \ . \tag{2.27}$$

Tyto operátory tvoří Lieovu algebru so(2,1). Uvedené komutační relace jsou podobné relacím, které platí pro složky momentu hybnosti. Dále bude stručně ukázáno, jak k nim lze určitou transformací přejít. Předtím ještě definujeme posunovací operátory $\hat{T}_\pm$

$$\hat{T}_\pm = \hat{T}_1 \pm i\hat{T}_2 \ . \tag{2.28}$$

Je vidět, že platí

$$[\hat{T}_3, \hat{T}_\pm] = \pm\hat{T}_\pm \tag{2.29}$$

a že $\hat{T}_\pm$ generují spektrum operátoru $\hat{T}_3$. Vlastní funkce radiální složky hamiltoniánu vodíku-podobného atomu $R_{n,l}(r)$

$$H = \frac{1}{2}\left(p_r^2 + \frac{l(l+1)}{r^2}\right) - \frac{1}{r} \tag{2.30}$$

jsou také vlastními funkcemi operátoru $\hat{T}_3$,

$$\hat{T}_3 R_{n,l}(r) = n R_{n,l}(r) \ . \tag{2.31}$$

Operátory $\hat{T}_\pm$ pak generují spektrum [2]

$$T_\pm R_{n,l} = \sqrt{(n \pm l \pm 1)(n \mp l)} R_{n\pm1,l}(r) \ . \tag{2.32}$$

Uvažujme radiální souřadnici r a k ní sdruženou hybnost p_r, pak operátory $\hat{V}_1 = r, \hat{V}_2 = rp_r, \hat{V}_3 = rp_r^2 + l(l+1)/r$ splňují komutační relace (2.17), (2.18), (2.19). Operátory $\hat{T}_i$ pak mají tvar:

$$T_1 = \frac{1}{2}(rp_r^2 + \frac{l(l+1)}{r} - r) \ , \tag{2.33}$$

$$T_2 = rp_r \ , \tag{2.34}$$

$$T_3 = \frac{1}{2}(rp_r^2 + \frac{l(l+1)}{r} + r) \ . \tag{2.35}$$

Z uvedených rekurentních relací pro operátory $\hat{T}_i$ se dají odvodit relace, které platí pro radiální část integrálů (1.1).

2.2 Multipólový rozvoj

Použitím multipólového rozvoje

$$\frac{1}{r_{12}} = \frac{1}{r_2}\sum_{l=0}^{\infty}(\frac{r_1}{r_2})^l P_l(n_1, n_2) \ , \tag{2.36}$$

kde $r_1 < r_2$ a $P_l(x)$ jsou Laguerrovy polynomy, můžeme rovnici (1.1) separovat na radiální a úhlovou část. Úhlová část se dá upravit metodami popsanými v [8], radiální část pak přejde do tvaru

$$X^{l_{1i},l_{2i},l_{1j},l_{2j},l}_{n_{1i},n_{2i},n_{1j},n_{2j}}(\xi_{1i}, \xi_{2i}, \xi_{1j}, \xi_{2j}) \ =$$

---

[2] Operátory $\hat{T}_\pm$ generují vlastní funkce. Připomeňme že je li $\hat{f} : V \to V$ normální operátor $(\hat{f}\hat{f}^* = \hat{f}^*\hat{f})$, tak existuje ortonormální base V složená z vlastních vektorů operátoru $\hat{f}$.

$$
\begin{aligned}
&= \int_0^\infty dr_1 R_{n1_i,l1_i}(r_1\xi_{1i})R_{n1_j,l1_j}(r_1\xi_{1j})r_1^{l+2} \quad \times \\
&\times \int_{r_1}^\infty dr_2 R_{n2_i,l2_i}(r_2\xi_{2i})R_{n2_j,l2_j}(r_2\xi_{2j})r_2^{-l+1} \quad + \\
&\int_0^\infty dr_1 R_{n1_i,l1_i}(r_1\xi_{2i})R_{n1_j,l1_j}(r_1\xi_{1j})r_1^{-l+1} \times \\
&\times \int_{r_1}^\infty dr_2 R_{n2_i,l2_i}(r_2\xi_{2i})R_{n2_j,l_{2_j}}(r_2\xi_{2j})r_2^{l+2} \,. \qquad (2.37)
\end{aligned}
$$

2.3 Linearizace

Jednotlivé části integrálu (2.37) obsahují součiny radiálních funkcí stejné proměnné. Díky tomu lze tyto integrály zjednodušit tzv. linearizací. To jsme provedli dvěma způsoby, z nichž každý vede k trochu jiné struktuře diferenčních rovnic. Zmíněné diferenční rovnice získané prvním resp. druhým způsobem jsou si ekvivalentní, ale umožňují vlastní výpočet algoritmizovat různými způsoby.

2.3.1 Linearizace převedením na řešení hypergeometrických funkcí

Tento způsob převedení součinu dvou kulových funkcí na lineární kombinaci kulových funkcí je speciálním případem tzv. Wigner-Eckartova teorému. Dá se ukázat, že jeho analogie pro so(2,1) algebru má tvar

$$
\begin{aligned}
&r^p R_{n1,l1}(\xi_1 r)R_{n2,l2}(\xi_2 r) = \\
&= \sum_{n=l1+l2+1}^{n1+n2-1+p} (n_1,l_1,\xi_1,n_1,l_2,\xi_2|n)_p R_{n,l1+l2}((\xi_1+\xi_2)r) \;.(2.38)
\end{aligned}
$$

Pro speciální případ $p = 1$, $\xi_1 = 1$, $\xi_2 = 1$ jsme vyjádřili koeficienty lineární kombinace pomocí hypergeometrických funkcí.

$$
\begin{aligned}
&(n_1,l_1,1,n_1,l_2,1|n)_1 = \\
&= A^{l_1,l_2}_{n_1,n_2} c^{l_1,l_2}_{n_1,n_2,n_1+n_2-1-n} \sqrt{\frac{(n+l_1+l_2)!}{(n-1-l_1-l_2)!}} \,, \qquad (2.39)
\end{aligned}
$$

kde

$$
A^{l_1,l_2}_{n_1,n_2} = \frac{2^{1-n_1-n_2}(n_1+n_2-l_1-l_2-2)!(n_1+l_1n_2+l_2)!}{(n_1-l_1-1)!(n_2-l_2-1)!} \times
$$

$$\times\sqrt{\frac{(n_1-l_1-1)!}{(n_1+l_1)!}}\sqrt{\frac{(n_2-l_2-1)!}{(n_2+l_2)!}}\,. \quad (2.40)$$

Koeficienty $c^{l_1,l_2}_{n_1,n_2,n}$ jsou rovny

$$c^{l_1,l_2}_{n_1,n_2,n} = C^{l_1,l_2}_{n_1,n_2,n} - \frac{(n_1+n_2-l_1-l_2-2-n)}{(n_1+n_2+l_1+l2-n-1)}C^{l_1,l_2}_{n_1,n_2,n+1}\,. \quad (2.41)$$

Koeficienty $C^{l_1,l_2}_{n_1,n_2,n}$ pak mají tvar

$$\begin{aligned}C^{l_1,l_2}_{n_1,n_2,n} = {} & \frac{F(-n_1+l_1+1,-n;-n_1-n_2+l_1+l_2+2;2)}{(n_1+l_1+n_2+l_2-n-1)!n!}\times \\ & \times F(-n_1-l_1,-n;-n1-n2-l_1-l_2;2)\end{aligned} \quad (2.42)$$

pro $n \geq 0$, jinak 0. $F(\alpha,\beta;\gamma;z)$ je hypergeometrická funkce. Tento vzorec jsme získali ze vzorce pro součin dvou Laguerrových polynomů [9]

2.3.2 Linearizace algebraickou technikou

Při určení koeficientů $(n1,l1,\xi1,n1,l2,\xi2|n)_p$ v rovnici (2.38) se dá postupovat tak, že se rovnice (2.38) vynásobí $rR_{n',l'}(\xi r)$ a dalšími úpravami dostaneme

$$\begin{aligned}(n_1,l_1,\xi_1,n_1,l_2,\xi_2|n)_p\sqrt{(n_1-l_1-1)(n_1+l_1)} = {} \\ 2(n_1-1-\tfrac{\xi_1 n}{\xi})(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n_p) \\ -\sqrt{(n_1+l_1-1)(n_1-l_1-2)}(n_1-2,l_1,\xi_1,n_2,l_2,\xi_2|n)_p \\ +\tfrac{\xi_1}{\xi}\sqrt{(n+l')(n-l'-1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n-1)_p \\ +\tfrac{\xi_1}{\xi}\sqrt{(n-l')(n+l'+1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n+1)_p\,,\end{aligned} \quad (2.43)$$

kde $l' = l_1 + l_2$ a $\xi = \xi_1 + \xi_2$. Poslední rovnice se dá použít ke snižování kvantových čísel n_1 a n_2.

2.4 Rekurentní relace pro integrály

Dosazením (2.38) do (2.37) obdržíme

$$\begin{aligned}& X^{l_{1i},l_{2i},l_{1j},l_{2j},l}_{n_{1i},n_{2i},n_{1j},n_{2j}}(\xi_{1i},\xi_{2i},\xi_{1j},\xi_{2j}) = \\ & = \sum_{N1}\sum_{N2}(n_{1i},l_{1i},\xi_{1i},n_{1j},l_{1j},\xi_{1j}|N_1)_1(n_{2i},l_{2i},\xi_{2i},n_{2j},l_{2j},\xi_{2j}|N_2)_1\times\end{aligned}$$

$$\times \left(P^{L_1,L_2}_{N_1,N_2}(\xi_1,\xi_2) + P^{L_2,L_1}_{N_2,N_1}(\xi_2,\xi_1)\right)\sqrt{\frac{(N_1-L_1-1)!}{(N_1+L_1)!}} \times$$
$$\times\sqrt{\frac{(N_1-L_2-1)!}{(N_2+L_2)!}}\,, \tag{2.44}$$

kde $L_1 = l_{1i} + l_{1j}$, $L_2 = l_{2i} + l_{2j}$, $\xi_1 = \xi_{1i} + \xi_{1j}$, $\xi_2 = \xi_{2i} + \xi_{2j}$. P jsou integrály přes dvě radiální funkce

$$P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2) = \int_0^\infty \tilde{R}_{N_1,L_1}(\xi_1 r_1) r_1^{l+1} \int_{r_1}^\infty \tilde{R}_{N_2,L_2}(\xi_2 r_2) r_2^{-l} dr_2 dr_1\,, \tag{2.45}$$

kde byly zavedeny nenormalizované funkce $\tilde{R}$

$$\tilde{R}_{n,l}(r) = \sqrt{\frac{(n+l)!}{(n-l-1)!}}R_{n,l}(r)\,. \tag{2.46}$$

Použitím nenormalizovaných funkcí je možno z rovnic eliminovat iracionální faktory (viz [10]). V rovnici (2.44) jsme využili rovnosti

$$\int_0^\infty \tilde{R}_{N_1,L_1}(\xi_1 r_1) r_1^{l+1} \int_{r_1}^\infty \tilde{R}_{N_2,L_2}(\xi_2 r_2) r_2^{-l} dr_1 dr_2 =$$
$$\int_0^\infty \tilde{R}_{N_2,L_2}(\xi_2 r_1) r_1^{-l} \int_0^{r_1} \tilde{R}_{N_1,L_1}(\xi_1 r_2) r_2^{l+1} dr_1 dr_2\,. \tag{2.47}$$

Linearizací se dosáhne toho, že integrály přes čtyři funkce se dají napsat jako lineární kombinace integrálů přes dvě funkce. Pro integrály přes dvě funkce se dají odvodit snadno řešitelné rekurentní relace. Rekurentní relace svazující integrály s různými hodnotami N_2 mají tvar

$$\begin{aligned} -(N_2+L_2)P^{L_1,L_2,l}_{N_1,N_2-1}(\xi_1,\xi_2) + &\quad (N_2-L_2)P^{L_1,L_2,l}_{N_1,N_2+1}(\xi_1,\xi_2) \\ -2lP^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2) = &\quad -(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2)\,, \end{aligned} \tag{2.48}$$

$$(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2) = \int_0^\infty 2r^2 \tilde{R}_{N_1,L_1}(\xi_1 r)\tilde{R}_{N_2,L_2}(\xi_2 r) dr\,. \tag{2.49}$$

Rekurentní relace svazující integrály s různými hodnotami N_1 mají tvar

$$\begin{aligned} -(N_1+L_1)P^{L_1,L_2,l}_{N_1-1,N_2}(\xi_1,\xi_2) &\quad +(N_1-L_1)P^{L_1,L_2,l}_{N_1+1,N_2}(\xi_1,\xi_2) \\ +2(l+1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2) &\quad = (N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2)\,. \end{aligned} \tag{2.50}$$

Numericky stabilní řešení těchto relací lze dosáhnout dvěma způsoby: za prvé se rekurentní relace se dají řešit pomocí hypergeometrických funkcí (viz [11] a [12]), zadruhé k těmto relacím je možno odvodit ještě další relace, plynoucí z obecnější algebraické struktury so(4,2), která vede k obecnějším relacím pro radiální funkce (viz [10])

2.5 Aplikace na dvouelektronové atomy

Schrödingerova rovnice pro dvouelektronové atomy s pevným jádrem (v atomových jednotkách) má tvar

$$\left[-\frac{\nabla_1^2}{2}-\frac{\nabla_2^2}{2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\right]\psi=E\psi\ , \tag{2.51}$$

kde Z je protonové číslo. Po přeškálování $\vec{x}^{(i)} \to Z^{-1}\vec{x}^{(i)}$ komutuje tento hamiltonián s komponentami celkového momentu hybnosti.

$$\left[-\frac{\nabla_{(1)}^2}{2}-\frac{\nabla_{(2)}^2}{2}-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{Zr_{12}}\right]\psi=\frac{E}{Z^2}\psi \tag{2.52}$$

Přesnou vlnovou funkci můžeme rozvinout do bázových funkcí adaptovaných k symetrii

$$\begin{aligned}&\langle\vec{r_1},\vec{r_2}|k\rangle = R_{n_{1k},l_{1k}}(r_1\xi_{1k})R_{n_{2k},l_{2k}}(r_2\xi_{2k})\langle\vec{n_1},\vec{n_2}|(l_{1k},l_{2k},L,0)\rangle \pm \\ &(-1)^{L-l_{1k}-l_{2k}}R_{n_{1k},l_{1k}}(r_2\xi_{1k})R_{n_{2k},l_{2k}}(r_1\xi_{2k})\langle\vec{n_2},\vec{n_1}|(l_{1k},l_{2k},L,0)\rangle\ ,\end{aligned} \tag{2.53}$$

kde $R_{n,l}(\xi r)$ jsou radiální funkce (1.2). Výpočet maticových elementů operátoru (2.52) v bázi funkcí (2.53) se redukuje na výpočet dvouelektronových integrálů (1.1) nebo výpočet jednoelektronových integrálů. Jednoelektronové integrály jsou dvou typů. První z nich jsou překryvové integrály, které se redukují na tvar (2.49). Druhé obsahují Laplaceův operátor:

$$\begin{aligned}&\int d^3r R_{n_1,l_1}(\xi_1 r)Y_{l_1,m_1}(\vec{n})(-\frac{\nabla^2}{2})rR_{n_2,l_2}(\xi_2 r)Y_{l_2,m_2}(\vec{n}) = \\ &\xi_2\int_0^\infty rR_{n_1,l_1}(\xi_1/\xi_2 r)\frac{r}{2}\left(p_r^2+\frac{l_1(l_1+1)}{r_2}\right)R_{n_2,l_1}(r)dr = \\ &\sqrt{\frac{(n_1-l_1-1)!(n_2-l_1-1)!}{(n_1+l_1)!(n_2+l_2)!}}\xi_2(n_1,l_1,\frac{\xi_1}{\xi_2}|\frac{T_3}{2}+\frac{T_++T_-}{4}|n_2,l_1,1)\ .\end{aligned} \tag{2.54}$$

Výsledné maticové elementy se (viz [10], [11]) redukují na výpočet překryvových integrálů

$$(N_1, L_1, \xi_1 | N_2, L_2, \xi_2) = \int_0^\infty r \tilde{R}_{N_1,L_1}(\xi_1 r) \tilde{R}_{N_2,L_2}(\xi_2 r) dr \ . \qquad (2.55)$$

Tyto integrály jsou relativně snadno spočitatelné, viz [10].

2.5.1 Numerické experimenty

V této části jsou shrnuty číselné výsledky numerických experimentů prováděných na atomu helia. Hlavním smyslem numerických experimentů byla tvorba podkladů pro odvození příslušných rekurentních relací (2.48, 2.49, 2.50) ve tvaru, který je numericky stabilní a výpočetně efektivní, následné otestování správnosti a nalezení efektivního a numericky stabilního algoritmu výpočtu hodnot hypergeometrických funkcí. Je třeba se také zmínit o otázce stínících konstant ξ_1 a ξ_2. Hlavní pozornost byla věnována otázce výpočtu integrálů. Stínící konstanty ξ_1 a ξ_2 je možno vhodně optimalizovat, aby se dosáhlo rychlé konvergence CI. V literatuře zatím nebyla nalezena systematická analýza týkající se těchto konstant, hledání jejich optimalizovaných hodnot je zatím obtížný úkol. Je potřeba rozlišit minimálně dva možné případy: Pro monoexcitované stavy 2^3S a 2^3P používáme $\xi_{1_k} = 1$ a $\xi_{2_k} = 1 - 1/Z$. V ostatních případech uvažujeme $\xi_{1_k} = \xi_{2_k} = 1$. Tyto hodnoty byly numericky ověřeny výpočtem CI s 50 bázovými funkcemi.

V tabulce (2.1) je vidět závislost vypočtené variační energie základního stavu atomu helia získaného diagonalizací zobecněného vlastního problému na počtu zahrnutých stavů, tj. na velikosti výřezu matice. V tabulce (2.2) je stejná závislost pro stav 2^3S a v tabulce (2.3) pro stav 2^3P. Pro základní stav konverguje energie v závislosti na řádu matice poněkud pomaleji. Energie stavů 2^3S a 2^3P konverguje lépe. Pro tyto stavy jsme dosáhli chyby menší než $1 \cdot 10^{-6}$, což je vzhledem k jednoduchosti použité báze dobrý výsledek.

Tabulka 2.1: Variační energie E_N základního stavu helia získaná diagonalizací zobecněného problému vlastních hodnot (2.52) pro dané N. Řád odpovídá řádu výřezu matice. ΔE značí rozdíl $E_N - E_{N-1}$. Přesná hodnota je -2.903724373 [5].

N	řád	E_N	ΔE
1	10	-2.8725067	
2	30	-2.8975136	$-0.25\ 10^{-1}$
3	60	-2.9009036	$-0.33\ 10^{-2}$
4	99	-2.9020298	$-0.11\ 10^{-2}$
5	146	-2.9025655	$-0.53\ 10^{-3}$
6	200	-2.9028682	$-0.30\ 10^{-3}$
7	260	-2.9030582	$-0.18\ 10^{-3}$
8	325	-2.9031862	$-0.12\ 10^{-3}$
9	394	-2.9032773	$-0.91\ 10^{-4}$
10	466	-2.9033447	$-0.67\ 10^{-4}$
11	540	-2.9033962	$-0.51\ 10^{-4}$
12	586	-2.9034357	$-0.39\ 10^{-4}$
13	632	-2.9034672	$-0.31\ 10^{-4}$
14	678	-2.9034922	$-0.24\ 10^{-4}$
15	724	-2.9035120	$-0.19\ 10^{-4}$
16	770	-2.9035277	$-0.15\ 10^{-4}$
17	816	-2.9035404	$-0.12\ 10^{-4}$
18	862	-2.9035508	$-0.10\ 10^{-4}$

Tabulka 2.2: To samé jako v Tabulce 2.1, ale pro 2^3S stavy. Přesná hodnota je -2.175229378 [5].

N	řád	E	ΔE
1	17	-2.174245506	
2	47	-2.175088716	-0.84 10^{-3}
3	86	-2.175208569	-0.11 10^{-3}
4	130	-2.175221935	-0.13 10^{-4}
5	175	-2.175225653	-0.37 10^{-5}
6	232	-2.175227182	-0.15 10^{-5}
7	288	-2.175227945	-0.76 10^{-6}
8	340	-2.175228372	-0.42 10^{-6}
9	401	-2.175228626	-0.25 10^{-6}
10	456	-2.175228790	-0.16 10^{-6}
11	502	-2.175228901	-0.11 10^{-6}
12	537	-2.175228977	-0.75 10^{-7}
13	562	-2.175229025	-0.47 10^{-7}

Tabulka 2.3: To samé jako v tabulce 2.1, ale pro 2^3P stavy. Přesná hodnota je -2.133164181 [5].

N	řád	E	ΔE
1	15	-2.131319860	
2	54	-2.132970321	-0.16 10^{-2}
3	106	-2.133129547	-0.15 10^{-3}
4	158	-2.133151474	-0.21 10^{-4}
5	224	-2.133157958	-0.64 10^{-5}
6	292	-2.133160583	-0.26 10^{-5}
7	368	-2.133161872	-0.12 10^{-5}
8	450	-2.133162588	-0.71 10^{-6}
9	521	-2.133163013	-0.42 10^{-6}
10	594	-2.133163291	-0.27 10^{-6}
11	672	-2.133163480	-0.18 10^{-6}
12	740	-2.133163610	-0.12 10^{-6}
13	798	-2.133163699	-0.89 10^{-7}

Kapitola 3

Diskuse a závěr

3.1 Diskuse výsledků

Jak bylo uvedeno výše, radiální část integrálů (1.1) je možno počítat dvěma způsoby. První možnost je převedení integrálů na výpočet hypergeometrických funkcí (2.38, 2.39), druhá možnost je požít rekurentních relací (2.38, 2.43). Níže budou diskutovány obě možnosti.

První variantu jsme zkoušeli pro případ, kdy stínící konstanty ξ_1 a ξ_2 byly stejné [11, 12]. V tomto případě se ve všech vztazích vyskytují hypergeometrické [1] funkce se základem 2. Zobecnění pro případ různých stínících konstant je poměrně snadno proveditelné, nicméně jsme se jím z časových důvodů nezabývali.

Výhody a nevýhody této varianty jsou následující. Při pohledu na vztahy pro maticové elementy (2.39,2.40, 2.41, 2.42) je zřejmé, že tyto elementy lze počítat na sobě zcela nezávisle. To znamená, že maticové elementy je možno počítat zcela paralelně. Výhoda tohoto postupu je, že při současném stavu výpočetní techniky je podstatně snazší provádět mnoho nezávislých výpočtů paralelně, než jediný výpočet mnohonásobně vyšší rychlostí. Tento postup však klade vysoké nároky na numerickou přesnost vypočítaných hodnot hypergeometrických funkcí. Značná část úsilí proto byla věnována problému výpočtu hodnot hypergeometrických funkcí. Tyto funkce

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[1] Hypergeometrická funkce viz [1] se obvykle značí $F(a,b;c;z)$, kde z je takzvaný základ. Gaussova řada hypergeometrické funkce je definována vztahem $F(a,b;c;z) = \sum_{n=0}^{\infty} \frac{(a)_n (b)_n}{(c)_n} \frac{z^n}{n!}$. Poznamenejme, že zvolení vhodného bodu, ve kterém provádíme rozvoj, má zásadní vliv na numerickou stabilitu výpočtu.

jsme se nejprve pokoušeli počítat z definice [1] a z Gaussových relací pro hypergeometrické funkce. Tento postup však uspokojivě funguje jen v racionální aritmetice [13]. V aritmetice s konečnou přesností dává často nepřesné výsledky. Po mnoha různých pokusech jsme nakonec vyvinuli algoritmus výpočtu popsaný v [12]. Tento algoritmus dává zatím nejpřesnější numerické hodnoty hypergeometrických funkcí v širokém rozsahu argumentů a je značně efektivní.

Druhá varianta je rekurzivní výpočet [10]. Tato možnost byla rozpracována zcela obecně, tj. i pro různé stínící konstanty. Samotná rekurzivní procedura výpočtu však neřeší principiálně problém numerické stability. Jeden z hlavních výsledků této práce je proto nalezení takových rekurentních relací, které vykazují vysokou numerickou stabilitu. Rekurzivní výpočet využívá k nalezení určitého maticového elementu maticové elementy s blízkými hodnotami kvantových čísel. Tento výpočet nelze provádět s takovou mírou paralelizace, jaké se dalo dosáhnout v předchozí variantě, nicméně výše popsané rekurentní relace je možno částečně paralelizovat. Poslední možnost zatím nebyla z časových důvodů rozpracována do detailu.

Výhoda vyvinutého algoritmu vynikne při výpočtu spekter víceelektronových atomů. Předběžné testy provedené na atomu helia ukazují, že metoda a její programová implementace je zcela korektní a dává výsledky, které souhlasí s jinými teoretickými výpočty a experimenty.

3.2 Hlavní výsledky práce

Hlavní výsledky této práce jsou:

1. linearizace součinu dvou radiálních funkcí a nalezení numericky stabilní metody výpočtu koeficientů lineární kombinace [11, 10],
2. odvození numericky stabilních rekurentních relací pro redukované integrály (2.48, 2.49, 2.50) [10],
3. zjištění, že redukované integrály (2.37) a koeficienty lineární kombinace (2.38, 2.39) lze vyjádřit prostřednictvím hypergeometrických funkcí [11],

4. nalezení numericky stabilní metody výpočtu hypergeometrických funkcí [12],
5. vývoj programu pro výpočet energií atomu He [12, 10],
6. spočtení velmi přesných hodnot energií atomu He [10].

3.3 Závěr a výhledy do budoucna

Chtěli bychom rozpracovat do detailu body 3. a 4. uvedené mezi hlavními výsledky. Dále chceme rozšířit metodu na relativistické radiální funkce (funkce, jež jsou řešením Diracovy rovnice pro atom vodíku). Kromě toho chceme aplikovat vyvinutou metodu na výpočet CI více-elektronových atomů, a tyto výsledky pak dále použít na zjištění vlivu slabých interakcí na atomová spektra. Uvažujeme také o rozšíření metody na dvoucentrové integrály.

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The use of so(2,1) algebra for the evaluation of atomic integrals: The study of two-electron atoms

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The use of the so(2,1) algebra for the study of the two-electron atoms is suggested. The radial part of the two-electron function is expanded into the products of the one-electron functions. These one-electron functions form complete, entirely discrete set and are identified as the eigenfunctions of one of the generators of the so(2,1) algebra. By applying this algebra we are able to express all the matrix elements in analytic and numericaly stable form. For matrix elements of the two-electron interaction this is done in three steps, all of them completely novel from the methodological point of view. First, repulsion integrals over four radial functions are written as a linear combination of the integrals over two radial functions and the coefficients of the linear combination are given in terms of hypergeometric functions. Second, combining algebraic technique with the integration by parts we derive recurrence relations for the repulsion integrals over two radial functions. Third, the derived recurrence relations are solved analytically in terms of the hypergeometric functions. Thus we succeed in expressing the repulsion integrals as rational functions of the hypergeometric functions. In this way we resolve the problem of the numerical stability of calculation of the repulsion integrals. Finally, as an illustration, the configuration interaction calculation of the lowest lying states of the He atom is discussed. *© 2004 American Institute of Physics.*
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I. INTRODUCTION

Two-electron atoms (like He, H^-, Li^+) are of great importance for their relative simplicity. There are primarily three interesting problems to be studied on the two-electron atoms. First, since the nonrelativistic Schrödinger equation can be solved very accurately for the ground as well as low excited states,[1–13] the relativistic and QED effects can be taken into account[13–18] and compared to the experiment.[19–22] This yields together with the study of the hydrogenlike atoms precise test of QED as a fundamental theory of the interaction of the electrically charged particles.[23–25] The second interesting point is the study of resonances.[26–28] This was stimulated by the experimental discovery of the strong correlation effects in the doubly excited states of helium[29] and led to new theoretical concepts, like approximate quantum numbers[30–32] and others. For an excellent review of these methods, see Ref. 33. Third, if the many-electron wave function is searched for in the form of expansion of a properly symmetrized product of the one-electron functions all the necessary matrix elements can be reduced either to one- or two-electron matrix elements whatever the number of the electrons involved. Therefore, if we find an effective method of calculating these matrix elements for the two-electron atoms, this method can be directly applied to *all* atoms and to the simplest molecules where it is physically reasonable to use orbitals localized at one center.

For low lying states of the two-electron atoms with low nuclear charge, the best approach is the one based on the use of the explicitly correlated functions.[1–11,13] This method consists of considering the interelectronic distance r_{12} as one of the coordinates. For example, for the S-states of helium, the two electron wave function is considered as a function of three variables r_1, r_2, and r_{12}, $\psi=\psi(r_1,r_2,r_{12})$. However, the disadvantage of this method is that transition to the three-electron atoms is very difficult[34] and increasing the number of the electrons further the method quickly loses its attractivity. Therefore, the method is not generally considered as a suitable tool for solving the many-electron problem.

The most accurate available method applicable for many electron problems is the configuration interaction method (CI) (see e.g., Refs. 35, 36). This method has been applied on the two-electron atoms either for finding some general trends of behavior of correlation energy like its angular dependence, optimization of the screening constant, and so on[37–44] or in combination with the complex scaling method (see, e.g., Ref. 45) for a description of resonances.[26–28,31,32]

However, the problem is when one wants to perform very large scale CI calculation to get very accurate results. Then one encounters what is usually refered to as the effect of linear dependence of the basis set. Due to numerical errors, for large basis sets the linear independence of the basis functions is lost. Thus, from some point the inclusion of more basis functions does not improve the variational results. To avoid this, one should keep the basis functions orthogonal. However, this requirement causes the highly excited functions to have large number of nodes and to change their sign frequently. That leads to the numerical instability of the calculation of the repulsion integrals.

This effect is quite general and appears also in the case of the explicitely correlated functions. However, here the convergence of the method is so fast that very accurate results are obtained before the problem appears.

To ensure numerical stability for the large scale CI calculations nonanalytic types of the basis functions like B-splines[12] or piecewise polynomials[41] or analytic types with many parameters[28] were invoked.

The aim of this paper is to suggest an efficient analytic method for calculating the one- and two-electron matrix elements applicable to all atoms and with numerical stability under control.

In this paper, a great deal of attention is devoted to the calculation of the repulsion integrals and the numerical stability of such a procedure. We expand the two-electron wave function into the symmetrized product of the complete, entirely discrete one-electron basis set. This basis set is in literature often refered to as a Sturmian one and its use goes back to the classical paper of Hylleraas.[46] However, in contrast to the usual treatment we identify these basis functions as the eigenfunction of one of the generators of the so(2,1) algebra.[47–52] This algebra is used for the calculation of the radial integrals appearing in the multipole expansion. We first introduce an analog to the Wigner–Eckart theorem for the so(2,1) algebra, i.e., we write the product of two radial functions as a linear combination of the radial functions. The coefficients of the linear combination can be expressed in terms of the hypergeometric functions. In this way we reduce the two-dimensional integration over four radial functions to the two-dimensional integration over two radial functions. Combining commutations relations of the so(2,1) algebra and analytic integration by parts we derive the reccurence relations for the integrals over two radial functions. In this way we reduce all the integrals to the integrals over nodeless functions. These integrals are calculated analytically. Finally, the derived reccurence relations are solved analytically in terms of the hypergeometric functions. Thus, we are able to express all the repulsion integrals as rational functions of the hypergeometric functions. Succeeding in this, this paper represents the solution of the problem of the numerical instability for the large scale CI calculations.

The problem considered in this paper was already tackled in Ref. 53. For the following reasons we believe that our solution is better suited for the computational purposes than that given in Ref. 53. First, when writing the products of the Laguerre polynomials as a linear combination of the Laguerre polynomials we succeded in expressing the coefficients of the linear combination in terms of the hypergeometric functions. Second, our recurrence relations for the integrals are much more simpler than that derived in Ref. 53. Third, we were able to solve them in terms of the hypergeometric functions. In this way all possible numerical instabilities are localized into the calculation of the well-known hypergeometric functions. These functions were thoroughly investigated by mathematicians and are known for long time. Once the values of these functions are calculated, the computation can be run in the double presicion arithmetics. In Ref. 53, the numerically unstable parts of the calculation had to be performed in integer arithmetics. On the other hand, at the present stage, the method described in this paper is less general than that given in Ref. 53. Possible generalizations of our method are indicated in the conclusions and will be described in detail in the forthcoming paper.

The paper is organized as follows: First, the algebraic solution of the hydrogen atom by means of the so(2,1) Lie algebra is described. Second, the problem of the helium atom is put into the form suitable for the use of so(2,1) algebra. Then we turn to the calculation of the repulsion integrals. Relying on the usual multipole expansion and integrating out the angular degrees of freedom in the usual manner, we concentrate on the calculation of the radial integrals. The two methods for calculation of the radial integrals are described. The first one consists of the expansion of the radial functions into the Slater-type orbitals, i.e., into the products of the exponential function and power of r. It is shown that this method is numerically unstable and reason of the instability is clarified. The second, "quasialgebraic" method is that described above. Finally, as an illustration, the CI calculation for the lowest lying states of helium atom is made and the optimization of the screening constant is discussed.

We would like to stress that we are not going to compete with the techniques using explicitly correlated functions. We apply the method for the states where CI is known to be converging very slowly to see numerical stability of our computation of the integrals. It is reasonable to expect that for other states the performance of the method will be better.

II. ALGEBRAIC TREATMENT OF THE HYDROGEN ATOM

In this section we introduce the so(2,1) algebra and show its use for the solution of the Schrödinger equation for hydrogen atom. For more detailed discussion see, e.g., Ref. 47. We adopt the same notation as that in Refs. 47 and 48.

Let us consider the Schrödinger equation for the hydrogen atom in atomic units

$$\left[-\frac{\nabla^2}{2}-\frac{1}{r}\right]\psi=E\psi. \tag{1}$$

The key idea for solving this equation algebraically is to transform this equation into the equation for the eigenvalues n of the operator T_3

$$T_3|l,n\rangle=n|l,n\rangle, \tag{2}$$

where the operator T_3 equals

$$T_3=\frac{1}{2}\left(rp_r^2+\frac{l(l+1)}{r}+r\right). \tag{3}$$

Here p_r is the conjugated radial momentum

$$p_r=-i\left(\frac{d}{dr}+\frac{1}{r}\right), \tag{4}$$

$l(l+1)$ is the eigenvalue of L^2, the square of the angular momentum and n is the principal quantum number (see below).

Equation (1) can be transformed to Eq. (2) as follows. Using the expression for the Laplace operator in the spherical coordinates

$$\nabla^2=p_r^2+\frac{L^2}{r^2}, \tag{5}$$

multiplying Eq. (1) by r and making the scaling transformation $r\to nr$ we get

$$\left[\frac{1}{2}r\left(p_r^2+\frac{L^2}{r^2}\right)-n^2Er\right]\psi=n\psi. \tag{6}$$

We separate the angular and radial degrees of freedom

$$\langle\mathbf{x}|\psi\rangle=\langle r|l,n\rangle\langle\mathbf{n}|l,m\rangle, \tag{7}$$

where $\mathbf{n}$ is a unit vector pointing in arbitrary direction and $\langle\mathbf{n}|l,m\rangle$ are spherical harmonics, the eigenfunctions of the square and the third component of the angular momentum, L^2 and L_3, respectively. Setting

$$E=-\frac{1}{2n^2}, \tag{8}$$

Eqs. (2) and (6) are the same.

The advantage of this reformulation of the problem of the hydrogen atom is that first, as we show below, the problem of the eigenvalues of the operator T_3 can be solved purely algebraically, second, the spectrum of the operator T_3 is purely discrete. Therefore, this operator is much more advantageous for description of bound atomic states than the usual operator in Eq. (1).

The eigenvalues of the operator T_3 can be obtained by observation that T_3 and the operators

$$T_1=\frac{1}{2}\left(rp_r^2+\frac{l(l+1)}{r}-r\right) \tag{9}$$

and

$$T_2=rp_r \tag{10}$$

are closed under the commutation and form the so-called so(2,1) Lie algebra

$$[T_1,T_2]=-iT_3, \tag{11}$$

$$[T_2,T_3]=iT_1, \tag{12}$$

and

$$[T_3,T_1]=iT_2. \tag{13}$$

Proceeding in analogy with the usual treatment of the so(3) algebra of the components of the angular momentum we introduce the ladder operators

$$T_\pm=T_1\pm iT_2. \tag{14}$$

From the commutation relations (12) and (13) we get

$$[T_3,T_\pm]=\pm T_\pm. \tag{15}$$

Applying the last equation to the eigenvectors $|l,n\rangle$ we get after some manipulation

$$T_3(T_\pm|l,n\rangle)=(n\pm1)(T_\pm|l,n\rangle). \tag{16}$$

It is clear from the last equation that the vectors $T_\pm|l,n\rangle$ are the eigenvectors of the operator T_3 with the eigenvalues corresponding to $n\pm1$. Therefore, we can write

$$T_\pm|l,n\rangle=\alpha^\pm(l,n)|l,n\pm1\rangle, \tag{17}$$

where $\alpha^{\pm}(l,n)$ are numbers specified as follows. From Eqs. (14), (11), (9), (10), and (3) we get successively

$$T_+T_- = T_1^2+T_2^2+i[T_2,T_1] = T_1^2+T_2^2-T_3 = T_3^2-l(l+1)-T_3. \tag{18}$$

Applying the last equation to the eigenvectors $|l,n\rangle$ we get from Eqs. (2) and (17)

$$\alpha^+(l,n-1)\alpha^-(l,n) = n^2-n-l(l+1) = (n+l)(n-l-1). \tag{19}$$

Requiring that the spectrum of the operator T_3 is bounded from below, i.e., there exists some $n_{\min}$ such that

$$T_-|l,n_{\min}\rangle = 0, \tag{20}$$

we get from Eq. (19) that $\alpha^-(l,n_{\min})=0$. This implies

$$n_{\min} = l+1. \tag{21}$$

Therefore, the eigenvalue spectrum of the operator T_3 starts at $n=l+1$ and then increases by 1 up to the infinity. Since the energy E is given by Eq. (8) we identify n with the usual principal quantum number.

To determine the numbers $\alpha^{\pm}(l,n)$ uniquely we require that the eigenvectors $|l,n\rangle$ are normalized ($\langle l,n|l,n\rangle = 1$). It leads to the following solution of Eq. (19):[48]

$$\alpha^+(l,n-1) = \alpha^-(l,n) = \sqrt{(n+l)(n-l-1)}. \tag{22}$$

For further considerations, let us show how the matrix elements of the radial coordinate r can be obtained. The radial coordinate r can be expressed as the difference of the operators T_3 and T_1 [see Eq. (3) and (9)]. From Eqs. (14), (17), and (22) we get that the operator r acts on the states $|l,n\rangle$ as follows (see, e.g., Ref. 48)

$$r|l,n\rangle = -\tfrac{1}{2}\sqrt{(n+l)(n-l-1)}|l,n-1\rangle + n|l,n\rangle - \tfrac{1}{2}\sqrt{(n+l+1)(n-l)}|l,n+1\rangle. \tag{23}$$

III. ALGEBRAIC TREATMENT OF THE HELIUM ATOM

In this section we first transform the Schrödinger equation into the form suitable for the use of the so(2,1) algebra. Next we turn our attention to the symmetry adaptation of the wave function. Relying on the multipole expansion, we separate angular and radial degrees of freedom in the conventional manner. We note that one of the alternatives to such an approach was recently suggested in Ref. 57. Finally, we integrate out the angular part and derive the expression for the radial integrals.

A. Schrödinger equation

The Schrödinger equation for the two-electron atoms in atomic units takes the form

$$\left[-\frac{\nabla_{(1)}^2}{2}-\frac{\nabla_{(2)}^2}{2}-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\right]\psi = E\psi, \tag{24}$$

where Z is the charge of the nucleus and r_{12} denotes the interelectronic distance.

By scaling the coordinates of the electrons $\mathbf{x}^{(i)} \to \eta Z^{-1}\mathbf{x}^{(i)}$, $i=1,2$, we get an equivalent equation

$$\left[-\frac{\nabla_{(1)}^2}{2}-\frac{\nabla_{(2)}^2}{2}-\frac{\eta}{r_1}-\frac{\eta}{r_2}+\frac{\eta}{Z}\frac{1}{r_{12}}\right]\psi = \frac{\eta^2}{Z^2}E\psi. \tag{25}$$

Here, η is an arbitrary scaling parameter that can be subject to further optimization. Multiplying Eq. (25) by $r_1 r_2$, writing the energy E as

$$E=-\frac{Z^2}{\eta^2}+\Delta E \tag{26}$$

and using Eqs. (3) and (5) we rewrite Eq. (25) into the form

$$\left[r_1(T_3^{(2)}-\eta)+r_2(T_3^{(1)}-\eta)+\frac{\eta}{Z}r_1 r_2 r_{12}^{-1}\right]\psi=\frac{\eta^2}{Z^2}\Delta E r_1 r_2 \psi. \tag{27}$$

Since the matrix elements of the one-electron operators r_i and $T_3^{(i)}$ can be calculated from Eqs. (23) and (2), respectively, the only remaining matrix elements to be calculated are the matrix elements of the operator $r_1 r_2 r_{12}^{-1}$, i.e., the repulsion integrals. Before doing so, we turn our attention to the construction of the wave function.

B. Construction of the wave function

The two electron wave function $|\psi\rangle$ has to be antisymmetric with respect to the interchange of the electrons. In this paper we restrict ourselves to the calculation of the ground state energy. Since the spin part of the ground state wave function of the helium atom is antisymmetric, the space part has to be symmetric. Further, because of the spherical symmetry of the problem, the components and the square of the total angular momentum $\mathbf{L}=\mathbf{L}^{(1)}+\mathbf{L}^{(2)}$ commute with the Hamiltonian. It means that the Hamiltonian has the block structure and the states with different eigenvalues of L_3 and L^2 do not mutually interact. The ground state is the singlet state with $L=0$, where $L(L+1)$ is the eigenvalue of the operator L^2. Therefore, the angular part of the wave function equals

$$|(l,l)0\rangle=\sum_{m=-l}^{l}(l,m,l,-m|0,0)|l,m\rangle^{(1)}|l,-m\rangle^{(2)}. \tag{28}$$

Here, $(\,|\,)$ denotes the Clebsch–Gordan (CG) coefficients. It follows from the properties of CG coefficients that Eq. (28) is the only nonzero combination of the products of one-electron angular states yielding the state with $L=0$. It means that to characterize the angular part of the total wave function we need just one quantum number l. It also follows from the properties of CG coefficients that the linear combination is symmetric with respect to the interchange of the electrons. Therefore, we expand the exact wave function into the unperturbed wave functions as follows:

$$|\psi\rangle=\sum_{i=0}^{\infty}f_i|i\rangle, \tag{29}$$

where

$$|i\rangle=2^{-(1+\delta_{n_{i1},n_{i2}})/2}(|l_i,n_{i1}\rangle^{(1)}|l_i,n_{i2}\rangle^{(2)}+|l_i,n_{i2}\rangle^{(1)}|l_i,n_{i1}\rangle^{(2)})|(l_i,l_i)0\rangle. \tag{30}$$

Here, the states $|l,n\rangle$ are the eigenstates of the operator T_3 given by Eq. (2). The coefficients f_i will be determined from the diagonalization of Eq. (27).

C. Matrix elements

Now we describe how the matrix elements of the operator $r_1 r_2 r_{12}^{-1}$ among the functions (30) are calculated.

Projecting the states $|l,n\rangle$ onto the coordinate basis we get the radial functions $R_{n,l}(r)=\langle r|l,n\rangle$. Introducing the inner product

$$\langle l_1,n_1|l_2,n_2\rangle=\int_0^\infty dr\, r\, R_{n_1,l_1}(r)R_{n_2,l_2}(r) \tag{31}$$

the functions $R_{n,l}(r)$ are orthonormal for $l_1=l_2$, $\langle l_1,n_1|l_1,n_2\rangle=\delta_{n_1,n_2}$. We note that this inner product differs from the usual one by the factor r^{-1} in the integrand (see, e.g., Refs. 47, 48).

To separate the angular and radial degrees of freedom we expand r_{12}^{-1} in the multipole expansion

$$r_{12}^{-1}=\frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\mathbf{n}_1\cdot\mathbf{n}_2), \tag{32}$$

where $r_<=r_1$, $r_>=r_2$ if $r_1<r_2$ and $r_<=r_2$, $r_>=r_1$ if $r_1>r_2$. Here, the $P_l(x)$ denotes the Legendre polynomials. With the definition of the inner product (31) and multipole expansion (32) the matrix elements of $r_1r_2r_{12}^{-1}$ can be written as

$$\langle i|r_1r_2r_{12}^{-1}|j\rangle=2^{-(\delta_{n_{i1},n_{i2}}+\delta_{n_{j1},n_{j2}})/2}\sum_{l=|l_i-l_j|}^{l_i+l_j}\theta_{l_i,l_j,l}[X^{l_i,l_j,l}_{n_{i1},n_{i2},n_{j1},n_{j2}}+X^{l_i,l_j,l}_{n_{i1},n_{i2},n_{j2},n_{j1}}], \tag{33}$$

where l in the summation increases by 2.

Here, the angular part $\theta_{l_i,l_j,l}$ corresponds to the calculation of the matrix elements of the Legendre polynomials between the coupled states (28)

$$\theta_{l_i,l_j,l}=\langle(l_i,l_i)0|P_l(\mathbf{n}_1\cdot\mathbf{n}_2)|(l_j,l_j)0\rangle=(-1)^{l_i+l_j}\frac{[(2l_i+1)(2l_j+1)]^{1/2}}{2l+1}(l_i,0,l_j,0|l,0)^2. \tag{34}$$

This result is obtained with help of the algebraic angular-momentum methods (see e.g., Refs. 54–56). It follows from the properties of the CG coefficients that $\theta_{l_i,l_j,l}$ is zero unless $|l_i-l_j|\leqslant l\leqslant l_i+l_j$ and l_i+l_j+l is even. Therefore, the sum in Eq. (33) is not infinite and in fact contains only a few terms.

The radial part of the integration reads

$$\begin{aligned}X^{l_i,l_j,l}_{n_{i1},n_{i2},n_{j1},n_{j2}}&=\int_0^\infty dr_1\int_0^\infty dr_2 r_1^2r_2^2R_{n_{i1},l_i}(r_1)R_{n_{i2},l_i}(r_2)\frac{r_<^l}{r_>^{l+1}}R_{n_{j1},l_j}(r_1)R_{n_{j2},l_j}(r_2)\\&=\int_0^\infty dr_1R_{n_{i1},l_i}(r_1)R_{n_{j1},l_j}(r_1)r_1^{l+2}\int_{r_1}^\infty dr_2R_{n_{i2},l_i}(r_2)R_{n_{j2},l_j}(r_2)r_2^{-l+1}\\&\quad+\int_0^\infty dr_1R_{n_{i1},l_i}(r_1)R_{n_{j1},l_j}(r_1)r_1^{-l+1}\int_0^{r_1}dr_2R_{n_{i2},l_i}(r_2)R_{n_{j2},l_j}(r_2)r_2^{l+2}.\end{aligned} \tag{35}$$

The following section is devoted to the calculation of these integrals.

IV. CALCULATION OF THE RADIAL INTEGRALS

In this section that is the main part of the paper, two methods of the calculations of the radial integrals (35) are described. The first method is given in the Sec. IV A and is based on the reduction of the integrals to the integrals over the Slater-type orbitals. This method is essentially the same as that used in Ref. 37. This method is shown to be numerically unstable. The second method is described in the remaining three subsections. In the Sec. IV B the integrals over four radial functions are transformed to the integrals over two radial functions with help of the analog of Wigner–Eckart theorem for so(2,1) algebra. In Sec. IV C the recurrence relations for the remaining integrals over two radial functions are derived. In Sec. IV D these recurrence relations are solved analytically.

A. Expansion into the Slater-type orbitals

The expansion of the integrals into the Slater-type orbitals is based on the explicit form of the radial functions

$$R_{n,l}(r)=2\sqrt{\frac{(n-l-1)!}{(n+l)!}}e^{-r}(2r)^l L_{n-l-1}^{2l+1}(2r), \tag{36}$$

where $L_{n-l-1}^{2l+1}(2r)$ are generalized Laguerre polynomials (see, e.g., Refs. 59–61).

Using the explicit form of the Laguerre polynomials we can rewrite the radial functions $R_{n,l}(r)$ as the linear combination of the Slater-type orbitals, i.e., as the products of the exponential function and power of r

$$R_{n,l}(r)=2\sum_{q=0}^{n-l-1} d_{n,l,q}e^{-r}r^{q+l}, \tag{37}$$

where the coefficients $d_{n,l,q}$ equal

$$d_{n,l,q}=\sqrt{\frac{(n-l-1)!}{(n+l)!}}\frac{(n+l)!}{(n-l-1-q)!q!(2l+1+q)!}(-1)^q 2^{q+l}. \tag{38}$$

Inserting this expansion into the integrals (35) we obtain after some manipulation

$$\begin{aligned}X^{l_i,l_j,l}_{n_{i1},n_{i2},n_{j1},n_{j2}}={}&\sum_{q_{i1}=0}^{n_{i1}-l_i-1} d_{n_{i1},l_i,q_{i1}}\sum_{q_{i2}=0}^{n_{i2}-l_i-1} d_{n_{i2},l_i,q_{i2}}\sum_{q_{j1}=0}^{n_{j1}-l_j-1} d_{n_{j1},l_j,q_{j1}}\sum_{q_{j2}=0}^{n_{j2}-l_j-1} d_{n_{j2},l_j,q_{j2}}\\&\times[I^l_{q_{i1}+q_{j1}+l_i+l_j+1,q_{i2}+q_{j2}+l_i+l_j+1}+I^l_{q_{i2}+q_{j2}+l_i+l_j+1,q_{i1}+q_{j1}+l_i+l_j+1}],\end{aligned} \tag{39}$$

where

$$\begin{aligned}I^l_{a,b}&=2^4\int_0^\infty dr_1e^{-2r_1}r_1^{a-l}\int_0^{r_1}dr_2e^{-2r_2}r_2^{b+l+1}\\&=2^4\int_0^\infty dr_1e^{-2r_1}r_1^{b+l+1}\int_{r_1}^\infty dr_2e^{-2r_2}r_2^{a-l}\\&=(a-l)!2^{-1-2b-l-a}\sum_{q=0}^{a-l}\frac{(b+l+q+1)!}{q!}2^{-q}.\end{aligned} \tag{40}$$

This way of calculation of the integrals (35) suffers by numerical instability. For example, running the formula (39) between the states with $n_{i1}=21$, $n_{i2}=19$, $l_i=3$ and $n_{j1}=17$, $n_{j2}=23$, $l_j=1$ in the double precision arithmetics yields the totally meaningless result 10^{20} for both $l=2$ and $l=4$. The reason for the instability is the changing sign of the $d_{n,l,q}$ coefficients, Eq. (38), that causes cancellation errors (see also discussion in Ref. 53). These changes are related to the orthogonality of the Laguerre polynomials. There is, of course, possibility to relax the requirement of having the orthonormal system of the functions and to consider the radial wave functions in the form $\tilde{R}_{n,l}(r)=\tilde{U}_{n,l}e^{-r}r^{n-1}$. This system is complete as well as the system (36). The pertinent radial integrals (35) can then be calculated according to the formula (40) and the matrix elements of the operators in Eq. (27) are calculated easily as well. The problem of doing this is that the numerical instability is just moved from the calculation of the integrals (35) to the generalized eigenvalue problem (27). In the case of the nonorthogonal basis the matrix r_1r_2 on the right-hand side of Eq. (27) is not just quasitridiagonal, but full.

Therefore, we will solve the problem of the numerical stability on the level of calculation of the integrals (35).

B. "Wigner–Eckart theorem" for so(2,1) algebra

Looking at Eq. (35) we observe that there are always the products of the wave functions of the same variable (like $R_{n_{i1},l_i}(r_1)R_{n_{j1},l_j}(r_1)$) that enter into the integration. Therefore, in the first step we try to write the product of two radial functions as a linear combination of the radial functions. Here, we proceed analogously to the angular integration. This trick of writing the product of two spherical harmonics as a linear combination of the spherical harmonics is a special case of much more general theorem called Wigner–Eckart theorem (see e.g., Refs. 54–58). We found its analog for so(2,1) algebra to be

$$rR_{n_i,l_i}(r)R_{n_j,l_j}(r)=A^{l_i,l_j}_{n_i,n_j}\sum_{n=-1}^{n_i+n_j-l_i-l_j-2}c^{l_i,l_j}_{n_i,n_j,n}\sqrt{\frac{(n_i+n_j-n-1+l_i+l_j)!}{(n_i+n_j-n-l_i-l_j-2)!}}R_{n_i+n_j-n-1,l_i+l_j}(2r), \tag{41}$$

where the multiplicative factor $A^{l_i,l_j}_{n_i,n_j}$ equals

$$A^{l_i,l_j}_{n_i,n_j}=\frac{2^{1-n_i-n_j}(n_i+n_j-l_i-l_j-2)!(n_i+l_i+n_j+l_j)!}{(n_i-l_i-1)!(n_j-l_j-1)!}\sqrt{\frac{(n_i-l_i-1)!}{(n_i+l_i)!}}\sqrt{\frac{(n_j-l_j-1)!}{(n_j+l_j)!}}. \tag{42}$$

The coefficients $c^{l_i,l_j}_{n_i,n_j,n}$ of the linear combination read

$$c^{l_i,l_j}_{n_i,n_j,n}=C^{l_i,l_j}_{n_i,n_j,n}-(n_i+n_j-l_i-l_j-2-n)C^{l_i,l_j}_{n_i,n_j,n+1}, \tag{43}$$

where the coefficients $C^{l_i,l_j}_{n_i,n_j,n}$ are given as

$$C^{l_i,l_j}_{n_i,n_j,n}=\frac{F(-n_i+l_i+1,-n;-n_i-n_j+l_i+l_j+2;2)\,F(-n_i-l_i,-n;-n_i-n_j-l_i-l_j;2)}{(n_i+l_i+n_j+l_j-n-1)!n!} \tag{44}$$

for $n\geqslant 0$ and equal zero otherwise. Here, $F(\alpha,\beta;\gamma;z)$ denotes the hypergeometric function (see e.g., Refs. 59–61).

The formula (41) was derived from the identities for the Laguerre polynomials found in Ref. 59, namely Eq. (5) of Sec. 8.6.4 and Eq. (11) of Sec. 5.5.2.

It is evident from the orthonormality of the radial functions for $l_i=l_j$ that an expression like (41) has to exist. What is new here is the explicit form of the coefficients $c^{l_i,l_j}_{n_i,n_j,n}$.

Using Eq. (41) in the radial integrals (35) we rewrite them into the form

$$\begin{aligned}X^{l_i,l_j,l}_{n_{i1},n_{i2},n_{j1},n_{j2}}&=A^{l_i,l_j}_{n_{i1},n_{j1}}A^{l_i,l_j}_{n_{i2},n_{j2}}\sum_{n_1=-1}^{n_{i1}+n_{j1}-l_i-l_j-2}c^{l_i,l_j}_{n_{i1},n_{j1},n_1}\sum_{n_2=-1}^{n_{i2}+n_{j2}-l_i-l_j-2}c^{l_i,l_j}_{n_{i2},n_{j2},n_2}\\&\quad\times\sqrt{\frac{(n_{i1}+n_{j1}-n_1-1+l_i+l_j)!}{(n_{i1}+n_{j1}-n_1-l_i-l_j-2)!}}\sqrt{\frac{(n_{i2}+n_{j2}-n_2-1+l_i+l_j)!}{(n_{i2}+n_{j2}-n_2-l_i-l_j-2)!}}\\&\quad\times Q^{l_i+l_j,l}_{n_{i1}+n_{j1}-1-n_1,n_{i2}+n_{j2}-1-n_2},\end{aligned} \tag{45}$$

where $Q^{L,l}_{N_1,N_2}$ denotes the integrals over two radial functions

$$Q_{N_1,N_2}^{L,l}=Q_{N_1,N_2}^{+,L,l}+Q_{N_1,N_2}^{-,L,l}. \tag{46}$$

Here,

$$Q_{N_1,N_2}^{+,L,l}=\int_0^{\infty}dr_1R_{N_1,L}(2r_1)r_1^{l+1}\int_{r_1}^{\infty}dr_2R_{N_2,L}(2r_2)r_2^{-l} \tag{47}$$

and

$$Q_{N_1,N_2}^{-,L,l}=\int_0^{\infty}dr_1R_{N_1,L}(2r_1)r_1^{-l}\int_0^{r_1}dr_2R_{N_2,L}(2r_2)r_2^{l+1}. \tag{48}$$

Before proceeding further let us point out that once the values of the hypergeometric functions and factorials are calculated, Eq. (43) is numerically stable. Therefore, this step of the calculation, the reduction of the integrals over four radial functions to the integrals over two radial functions, is numerically stable. The next step is to find the stable way of calculation of the integrals (46)–(48).

C. Derivation of the reccurrence relations for the integrals

In this subsection, we derive the recurrence relations for the integrals (47) and (48).

To motivate our further considerations we note that when we expand the radial functions in the integrals (47) and (48) into the powers of r, Eq. (37), the numerical instabilities appear again. Obviously, to achieve numerical stabilization we have to treat the functions $R_{n,l}(2r)$ as one indivisible object. The functions $R_{n,l}(2r)$ are treated in this way, when applying algebraic approach. The ladder operators $T_{\pm}$ change the whole function $R_{n,l}(2r)$ into the other functions $R_{n\pm1,l}(2r)$. Therefore, in the following we try to apply these ladder operators to the radial functions. To do so, we have to combine this algebraic technique with the analytic integration by parts.

1. Elementary example

For the sake of transparency, let us first consider the integral

$$\int_0^{r_1}dr_2\,R_{N_2,L}(2r_2). \tag{49}$$

After we show the numerically stable way how to calculate this integral, we extend it to the integrals (47) and (48).

First, let us show that

$$\int_0^{r_1}dr_2\,r_2\left(\frac{d}{dr_2}+\frac{1}{r_2}\right)[R_{N_2,L}(2r_2)]=r_1R_{N_2,L}(2r_1). \tag{50}$$

The proof is elementary. Expanding the brackets on the left hand side we get

$$\int_0^{r_1}dr_2\,r_2\left(\frac{d}{dr_2}+\frac{1}{r_2}\right)[R_{N_2,L}(2r_2)]=\int_0^{r_1}dr_2\,R_{N_2,L}(2r_2)+\int_0^{r_1}dr_2\,r_2\frac{d}{dr_2}[R_{N_2,L}(2r_2)]. \tag{51}$$

Integrating the second term by parts

$$\int_0^{r_1}dr_2\,r_2\frac{d}{dr_2}[R_{N_2,L}(2r_2)]=[r_2R_{N_2,L}(2r_2)]_0^{r_1}-\int_0^{r_1}dr_2\,R_{N_2,L}(2r_2) \tag{52}$$

and inserting this term into Eq. (51) we get Eq. (50).

Second, we observe that the operator $r((d/dr)+(1/r))$ is up to the imaginary unit equal to the operator T_2, Eq. (10) and the operator T_2 can be expressed as the difference of the creation and annihilation operators T_+ and T_-, Eq. (14)

$$r\left(\frac{d}{dr}+\frac{1}{r}\right)=irp_r=iT_2=\frac{1}{2}(T_+-T_-). \tag{53}$$

Thus, from the algebraic side we see that the operator (53) acts on the radial functions as

$$\begin{aligned}r\left(\frac{d}{dr}+\frac{1}{r}\right)[R_{N_2,L}(2r)]=&\frac{1}{2}\sqrt{(N_2+L+1)(N_2-L)}R_{N_2+1,L}(2r)\\&-\frac{1}{2}\sqrt{(N_2+L)(N_2-L-1)}R_{N_2-1,L}(2r),\end{aligned} \tag{54}$$

where Eq. (17) was used.

Finally, combining the analytic result (50) with the algebraic one (54) we get the recurrence relation for the integrals (49)

$$\begin{aligned}&\frac{1}{2}\sqrt{(N_2+L+1)(N_2-L)}\int_0^{r_1}dr_2\,R_{N_2+1,L}(2r_2)-\frac{1}{2}\sqrt{(N_2+L)(N_2-L-1)}\int_0^{r_1}dr_2\,R_{N_2-1,L}(2r_2)\\&=r_1R_{N_2,L}(2r_1).\end{aligned} \tag{55}$$

With this reccurence relation we reduce the quantum number N_2 to $L+1$. The integral over nodeless function $R_{L+1,L}(2r_2)$ is calculated analytically according to Eq. (40). The advantage of the recurrence relation (55) is that calculating integral over $R_{N_2+1,L}(2r_2)$ from the integral over $R_{N_2-1,L}(2r_2)$ contains the sum of positive numbers and not the difference of two numbers. Therefore, it is numerically stable.

2. Recurrence relations for $Q^{-;L,l}_{N_1',N_2}$ connecting different values of N_2

Now, we extend the described procedure to the calculation of the integrals appearing in Eq. (48)

$$\int_0^{r_1}dr_2\,r_2^{l+1}R_{N_2,L}(2r_2). \tag{56}$$

The analytic aspect is the same. By the same calculation as for Eq. (50) we get

$$\int_0^{r_1}dr_2\,r_2\left(\frac{d}{dr_2}+\frac{1}{r_2}\right)[R_{N_2,L}(2r_2)r_2^{l+1}]=r_1^{l+2}R_{N_2,L}(2r_1). \tag{57}$$

From the algebraic side we can deal with the extra term r^{l+1} using the commutation relation[47]

$$[r^k,irp_r]=-kr^k \tag{58}$$

that holds for every integer $k>0$. Applying this operator identity for $k=l+1$ to the radial functions $R_{N_2,L}(2r)$ we get

$$\int_0^{r_1} dr_2\, ir_2p_{r_2}[R_{N_2,L}(2r_2)r_2^{l+1}] = \int_0^{r_1} dr_2\, r_2^{l+1} ir_2p_{r_2}[R_{N_2,L}(2r_2)] + (l+1)\int_0^{r_1} dr_2\, r_2^{l+1} R_{N_2,L}(2r_2). \tag{59}$$

Combining again the analytical result (57) with the algebraic results (54) and (59) we get

$$\begin{aligned} r_1^{l+2}R_{N_2,L}(2r_1) = {} & \frac{1}{2}\sqrt{(N_2+L+1)(N_2-L)}\int_0^{r_1} R_{N_2+1,L}(2r_2)r_2^{l+1}dr_2 \\ & -\frac{1}{2}\sqrt{(N_2+L)(N_2-L-1)}\int_0^{r_1} R_{N_2-1,L}(2r_2)r_2^{l+1}dr_2 \\ & +(l+1)\int_0^{r_1} R_{N_2,L}(2r_2)r_2^{l+1}. \end{aligned} \tag{60}$$

Finally, multiplying the last equation by $r_1^{-l}R_{N_1,L}(2r_1)$ and integrating from zero to infinity we obtain

$$\begin{aligned} \tfrac{1}{8}\langle L,N_1|r|L,N_2\rangle = {} & \tfrac{1}{2}\sqrt{(N_2+L+1)(N_2-L)}\,Q_{N_1,N_2+1}^{-,L,l} \\ & -\tfrac{1}{2}\sqrt{(N_2+L)(N_2-L-1)}\,Q_{N_1,N_2-1}^{-,L,l} + (l+1)Q_{N_1,N_2}^{-,L,l}, \end{aligned} \tag{61}$$

where we used Eqs. (31) and (48). Matrix elements of r are calculated from Eq. (23).

3. Recurrence relations for $Q_{N_1,N_2}^{-,L,l}$ connecting different values of N_1

To derive recurrence relations for $Q_{N_1,N_2}^{-,L,l}$ connecting the different values of N_1 we will need a slight modification of Eq. (57)

$$\begin{aligned} & \int_0^{\infty} dr_1\, r_1\left(\frac{d}{dr_1}+\frac{1}{r_1}\right)[r_1^{-l}R_{N_1,L}(2r_1)]\int_0^{r_1} dr_2\, R_{N_2,L}(2r_2)r_2^{l+1} \\ & = -\int_0^{\infty} dr_1\, r_1^2 R_{N_1,L}(2r_1)R_{N_2,L}(2r_1). \end{aligned} \tag{62}$$

This equation can be derived as follows. We expand the bracket on the left-hand side

$$\begin{aligned} & \int_0^{\infty} dr_1\, r_1\left(\frac{d}{dr_1}+\frac{1}{r_1}\right)[r_1^{-l}R_{N_1,L}(2r_1)]\int_0^{r_1} dr_2\, R_{N_2,L}(2r_2)r_2^{l+1} \\ & = \int_0^{\infty} dr_1\, r_1^{-l}R_{N_1,L}(2r_1)\int_0^{r_1} dr_2\, R_{N_2,L}(2r_2)r_2^{l+1} \\ & \quad + \int_0^{\infty} dr_1\, r_1\frac{d}{dr_1}[r_1^{-l}R_{N_1,L}(2r_1)]\int_0^{r_1} dr_2\, R_{N_2,L}(2r_2)r_2^{l+1} \end{aligned} \tag{63}$$

and integrate the second term by parts

$$\int_0^\infty dr_1\, r_1 \frac{d}{dr_1}[r_1^{-l} R_{N_1,L}(2r_1)] \int_0^{r_1} dr_2\, R_{N_2,L}(2r_2) r_2^{l+1}$$
$$= \left[r_1^{-l+1} R_{N_1,L}(2r_1) \int_0^{r_1} dr_2\, R_{N_2,L}(2r_2) r_2^{l+1} \right]_0^\infty - \int_0^\infty dr_1\, r_1^{-l} R_{N_1,L}(2r_1) \int_0^{r_1} dr_2$$
$$\times R_{N_2,L}(2r_2) r_2^{l+1} - \int_0^\infty dr_1\, r_1^2 R_{N_1,L}(2r_1) R_{N_2,L}(2r_1), \tag{64}$$

where we used the Newton formula for differentiation of the integral with respect to the upper bound. Since the boundary term vanishes, by inserting Eq. (64) into Eq. (63) we get Eq. (62).

Also the algebraic side of the calculation requires only slight modification of the previous case. Instead of the commutation relation (58) we use the commutation relation

$$[r^{-k}, irp_r] = -kr^{-k} \tag{65}$$

that is obtained from Eq. (58) by multiplying both sides by r^{-k}. Applying this operator identity to the radial functions $R_{N_1,L}(2r_1)$ for $k=l$ leads to

$$ir_1 p_{r_1}[r_1^{-l} R_{N_1,L}(2r_1)] = r_1^{-l} ir_1 p_{r_1}[R_{N_1,L}(2r_1)] - l r_1^{-l} R_{N_1,L}(2r_1). \tag{66}$$

We use the last equation in the integrand on the left hand side of Eq. (62), then apply Eq. (54), where we just replace N_2 by N_1. After some manipulation we get the sought reccurence relation

$$-\tfrac{1}{8}\langle L,N_1|r|L,N_2\rangle = \tfrac{1}{2}\sqrt{(N_1+L+1)(N_1-L)}\, Q^{-,L,l}_{N_1+1,N_2}$$
$$-\tfrac{1}{2}\sqrt{(N_1+L)(N_1-L-1)}\, Q^{-,L,l}_{N_1-1,N_2} - l Q^{-,L,l}_{N_1,N_2}. \tag{67}$$

4. Recurrence relations for the integrals $Q^{+,L,l}_{N_1,N_2}$

No new ideas are required to derive the recurrence relations for the integrals $Q^{+,L,l}_{N_1,N_2}$. Proceeding in analogy with the previous cases we derive recurrence relations connecting the integrals with different values of N_2,

$$-\tfrac{1}{8}\langle L,N_1|r|L,N_2\rangle = \tfrac{1}{2}\sqrt{(N_2+L+1)(N_2-L)}\, Q^{+,L,l}_{N_1,N_2+1}$$
$$-\tfrac{1}{2}\sqrt{(N_2+L)(N_2-L-1)}\, Q^{+,L,l}_{N_1,N_2-1} - l Q^{+,L,l}_{N_1,N_2} \tag{68}$$

and the recurrence relations connecting the integrals with different values of N_1,

$$\tfrac{1}{8}\langle L,N_1|r|L,N_2\rangle = \tfrac{1}{2}\sqrt{(N_1+L+1)(N_1-L)}\, Q^{+,L,l}_{N_1+1,N_2}$$
$$-\tfrac{1}{2}\sqrt{(N_1+L)(N_1-L-1)}\, Q^{+,L,l}_{N_1-1,N_2} + (l+1) Q^{+,L,l}_{N_1,N_2}. \tag{69}$$

It is immediately seen from Eqs. (61), (67), (68), and (69) that

$$Q^{+,L,l}_{N_1,N_2} = Q^{-,L,l}_{N_2,N_1}. \tag{70}$$

Through the derived recurrence relations all the needed integrals are reduced to the calculation of the integrals $Q^{+,L,l}_{L+1,L+1}$. These integrals can be calculated from Eq. (40),

$$Q_{L+1,L+1}^{+,L,l}=\frac{2^{-2+4L}}{(2L+1)!}I_{L,L}^{l}=2^{-1}(2L+1)!\,F(1,-L+l;-2L-1;2). \tag{71}$$

D. Solution of recurrence relations

To solve recurrence relations derived in the previous section it is advantageous to eliminate the irrational factors by introducing the unnormalized integrals

$$\tilde{Q}_{N_1,N_2}^{\pm,L,l}=4\sqrt{\frac{(N_1+L)!}{(N_1-L-1)!}}\sqrt{\frac{(N_2+L)!}{(N_2-L-1)!}}\,Q_{N_1,N_2}^{\pm,L,l}. \tag{72}$$

Then the recurrence relations take the form

$$\begin{aligned}-\sqrt{\frac{(N_1+L)!}{(N_1-L-1)!}}\sqrt{\frac{(N_2+L)!}{(N_2-L-1)!}}\langle L,N_1|r|L,N_2\rangle\\ =(N_2-L)\tilde{Q}_{N_1,N_2+1}^{+,L,l}-(N_2+L)\tilde{Q}_{N_1,N_2-1}^{+,L,l}-2l\tilde{Q}_{N_1,N_2}^{+,L,l}\end{aligned} \tag{73}$$

and

$$\begin{aligned}\sqrt{\frac{(N_1+L)!}{(N_1-L-1)!}}\sqrt{\frac{(N_2+L)!}{(N_2-L-1)!}}\langle L,N_1|r|L,N_2\rangle\\ =(N_1-L)\tilde{Q}_{N_1+1,N_2}^{+,L,l}-(N_1+L)\tilde{Q}_{N_1-1,N_2}^{+,L,l}+2(l+1)\tilde{Q}_{N_1,N_2}^{+,L,l}.\end{aligned} \tag{74}$$

The recurrence relations for $\tilde{Q}_{N_1,N_2}^{-,L,l}$ are obtained using Eq. (70).

1. Solution in the variable N_1

Because of Eq. (70) we can restrict our attention to the case $N_1 \geqslant N_2$. We note that the matrix elements $\langle L,N_1|r|L,N_2\rangle$ vanish whenever $|N_2-N_1|>1$, see Eq. (23). That means that for $N_1>N_2+1$ the recurrence relation (74) is homogenous. Since it is the three-term recursion relation we need two initial values of $\tilde{Q}_{N_1,N_2}^{+,L,l}$, namely $\tilde{Q}_{N_2+2,N_2}^{+,L,l}$ and $\tilde{Q}_{N_2+1,N_2}^{+,L,l}$ to determine the solution uniquely.

General solution of homogenous Eq. (74) is

$$\begin{aligned}\tilde{Q}_{N_1,N_2}^{+,L,l}&=g_1(N_2)F(N_1-L,-L+l+1;-2L;2)\\ &\quad+g_2(N_2)(-1)^{N_1-L-1}F(N_1-L,-L-l-1;-2L;2).\end{aligned} \tag{75}$$

We found this solution by realizing that the recurrence relation (74) can be transformed to the one of the relations between contigous hypergeometric functions (see, e.g., Ref. 61). This solution holds for all $N_1>N_2$ including the cases $N_1=N_2+2$ and $N_1=N_2+1$, that can be viewed as the initial conditions. In principle we could determine the functions $g_1(N_2)$ and $g_2(N_2)$ by considering Eq. (75) for $N_1=N_2+1$ and $N_1=N_2+2$. However, it is more advantageous to proceed in different way; to insert directly solution (75) into Eq. (73). This is done in the following paragraph.

2. Solution in the variable N_2

If we consider Eq. (73) for $N_1=N_2+2$ we obtain

$$(N_2-L)\tilde{Q}_{N_2+2,N_2+1}^{+,L,l}-2l\tilde{Q}_{N_2+2,N_2}^{+,L,l}-(N_2+L)\tilde{Q}_{N_2+2,N_2-1}^{+,L,l}=0. \tag{76}$$

Further, considering Eq. (73) for $N_1=N_2+3$ we get

$$(N_2-L)\tilde{Q}^{+,L,l}_{N_2+3,N_2+1}-2l\tilde{Q}^{+,L,l}_{N_2+3,N_2}-(N_2+L)\tilde{Q}^{+,L,l}_{N_2+3,N_2-1}=0, \tag{77}$$

and so on. It seen from these equations that the values of $\tilde{Q}^{+,L,l}_{N_1,N_2}$ for $N_2=N_1+1$ can be calculated from Eq. (76), the values of $\tilde{Q}^{+,L,l}_{N_1,N_2}$ for $N_2=N_1+2$ can be calculated from Eq. (77), and so on. Therefore, all the values of $\tilde{Q}^{+,L,l}_{N_1,N_2}$ for $N_1>N_2$ including the values $N_1=N_2+1$ and $N_1=N_2+2$ can be calculated from *homogenous* Eq. (73).

By inserting solution (75) into the homogenous equation (73) we get

$$\begin{aligned}&F(N_1-L,-L+l+1;-2L;2)[(N_2-L)g_1(N_2+1)-(N_2+L)g_1(N_2-1)-2lg_1(N_2)]\\&\quad+(-1)^{N_1-L-1}F(N_1-L,-L-l-1;-2L;2)[(N_2-L)g_2(N_2+1)\\&\quad-(N_2+L)g_2(N_2-1)-2lg_2(N_2)]=0.\end{aligned} \tag{78}$$

Requiring that this equation is satisfied for $N_1=N_2+1$ and $N_1=N_2+2$ the expression in the brackets have to vanish. It is the three-term recursion relation having the solution

$$\begin{aligned}g_i(N_2)=&\,g_i^{(1)}(-1)^{N_2-L-1}F(N_2-L,-L+l;-2L;2)\\&+g_i^{(2)}F(N_2-L,-L-l;-2L;2),\quad i=1,2.\end{aligned} \tag{79}$$

Thus, Eqs. (75) and (79) represent a general solution for $\tilde{Q}^{+,L,l}_{N_1,N_2}$ for all $N_1>N_2$. Four constants $g_i^{(j)}$, $i,j=1,2$ are determined from four values $\tilde{Q}^{+,L,l}_{L+i+j,L+j}$, $i,j=1,2$.

The solution for $\tilde{Q}^{-,L,l}_{N_1,N_2}$ is obtained by reversing the role of N_1 and N_2 in Eqs. (75) and (79). The constants $g_i^{(j)}$, $i,j=1,2$ are determined as in the previous case.

3. Final result

Proceeding in the way described above we arrive to the explicit solution for the integrals $\tilde{Q}^{\pm,L,l}_{N_1,N_2}$,

$$\begin{aligned}\tilde{Q}^{+,L,l}_{N_1,N_2}=&\,K(L,l)F(N_1-L,-L+l+1;-2L;2)[(-1)^{N_2+1-L}\\&\times F(N_2-L,-L+l;-2L;2)+F(N_2-L,-L-l;-2L;2)]\end{aligned} \tag{80}$$

and

$$\begin{aligned}\tilde{Q}^{-,L,l}_{N_1,N_2}=&\,K(L,l)(-1)^{N_1-L-1}F(N_1-L,-L+l;-2L;2)\times[(-1)^{N_2+1-L}F(N_2-L,-L-l-1;\\&-2L;2)+F(N_2-L,-L+l+1;-2L;2)].\end{aligned} \tag{81}$$

The constant $K(L,l)$ is in both cases the same and equals

$$K(L,l)=\frac{(2L+1)!}{F(2,-L+l+1;-2L;2)}\,\frac{L+1-(l+1)F(1,-L+l;-2L-1;2)}{F(1,-L+l;-2L;2)+F(1,-L-l;-2L;2)}. \tag{82}$$

These solutions hold for all $N_1>N_2$ and for all $L>l$. The solution for $L=l$ has very simple form

$$\tilde{Q}^{+,L,L}_{N_1,N_2}=0 \tag{83}$$

and

$$\tilde{Q}^{-,L,L}_{N_1,N_2}=(-1)^{N_2-N_1}\frac{(N_2+L)!}{(N_2-L-1)!}. \tag{84}$$

TABLE I. Labeling of the basis sets. States are ordered in accordance with the increasing unperturbed energies, i.e., in accordance with the sum of principal quantum numbers $n_{12}(i)=n_{i1}+n_{i2}$.

i	n_{i1}	n_{i2}	l_i	n_{12}
1	1	1	0	2
2	1	2	0	3
3	1	3	0	4
4	2	2	0	4
5	2	2	1	4
6	1	4	0	5
7	2	3	0	5
8	2	3	1	5

The solutions for $N_1=N_2$ for $N_1>L+1$ are obtained by considering Eq. (73) for $N_2=N_1-1$.

The explicit solution of reccurence relations given in this subsection finishes our way to the stable calculation of the radial integrals. The final solution of numerical stable calculation of the radial integrals is the use of Eq. (45), where the integrals $Q^{L,l}_{N_1,N_2}$ are calculated from Eqs. (46), (72), (80), (81), (83), and (84). Running these equations in the double precision arithmetics for $n_{i1}=21$, $n_{i2}=19$, $n_{j1}=17$, and $n_{j2}=23$ for different values of l_i, l_j, and l yields the relative error in the worst cases of the order 10^{-14}.

Finally, we would like to emphasize that all the hypergeometric functions appearing in Eqs. (44), (80), (81), and (82) are in fact polynomials, so the question of convergence of the corresponding series in their computation does not arise.

V. CONFIGURATION INTERACTION

As an illustration, we solve Eq. (27) variationally for the helium atom, i.e., for $Z=2$. It is well-known that the ground state of helium is one of the most difficult cases of calculation of the electron–electron correlation (see below), so we give this example to see the performance of the method under unfavorable circumstances. We label the basis vectors $|i\rangle$ in the way indicated in Table I. The states are ordered in such a way that the unperturbed energies increase, i.e., according to the sum of the hydrogen principal quantum numbers $n_{i1}+n_{i2}$. The truncated basis sets are characterized by the number n_{12} that denotes the maximum of the sums $n_{i1}+n_{i2}$ of the states included in the truncated basis sets. For example, the basis set characterized by $n_{12}=2$ includes all the states with $2\geqslant n_{i1}+n_{i2}$. This basis set is one-dimensional $\{|0,1\rangle^{(1)}|0,1\rangle^{(2)}|(0,0)0\rangle\}$. The basis set characterized by $n_{12}=3$ is two-dimensional: $\{|0,1\rangle^{(1)}|0,1\rangle^{(2)}|(0,0)0\rangle, 2^{-1/2}(|0,1\rangle^{(1)}|0,2\rangle^{(2)}+|0,2\rangle^{(1)}|0,1\rangle^{(2)})|(0,0)0\rangle\}$. Similarly, the basis set characterized by $n_{12}=4$ is five-dimensional, by $n_{12}=5$ eight-dimensional, and so on.

We note that our variational calculation corresponds to what is usually called the full CI with the successively increasing basis set.

The parameter η in Eq. (27) was optimized numerically by calculating the values of the energy for some discrete values of η and looking for the minimum of these discrete values. Results are shown in Table II.

We found that the parameter η with increasing basis set decreases, see Table II. This can be intuitively understood as follows. We have to build the atomic orbitals in such a way to describe the motion of the electrons properly, i.e., to obtain high probability of their appearence in the places where they "really" are. As we enlarge the basis sets the maximum of this probability is moving to the places more distant from the nucleus. Therefore, to get it to the proper place, close to the nucleus, the screening constant η has to decrease. Numerical analysis shows that the optimal screening constant η goes to zero roughly like n_{12}^{-1}. However, this analysis is not very reliable since the optimal screening constant η is determined with lower accuracy than the variational

TABLE II. The variational energy levels $E(\eta)$ of the ground state of helium obtained by diagonalization of the generalized eigenvalue problem (27) with the optimized choices of the parameter η. *order* denotes the order of the truncated matrix. The relative error is calculated with respect to the value -2.903724377 given in Ref. 8. ∞ denotes the extrapolated value, the extrapolation was made with respect to n_{12}^{-3}, see text for details.

n_{12}	Order	η	$E(\eta)$	Error $E(\eta)$ [%]
2	1	1.18518	−2.847656250000	1.930
3	2	1.18518	−2.847656250000	1.930
4	5	0.97196	−2.895444678791	0.285
5	8	0.94051	−2.897109123114	0.227
6	14	0.79681	−2.900714155920	0.103
7	20	0.76085	−2.901452790421	0.0782
8	30	0.68217	−2.902341254761	0.0476
9	40	0.64803	−2.902654772148	0.0368
10	55	0.59598	−2.902975741200	0.0257
28	1015	0.28285	−2.903681963068	0.00146
29	1120	0.27532	−2.903685852234	0.00132
30	1240	0.26782	−2.903689437387	0.00120
31	1360	0.26104	−2.903692451003	0.00109
32	1496	0.25431	−2.903695236574	0.00100
33	1632	0.24821	−2.903697608901	0.000928
34	1785	0.24206	−2.903699807464	0.000846
35	1938	0.23660	−2.903701701251	0.000780
36	2109	0.23126	−2.903703460890	0.000720
37	2280	0.22601	−2.903704991252	0.000667
38	2470	0.22129	−2.903706417162	0.000618
39	2660	0.21684	−2.903707667974	0.000575
40	2870	0.21223	−2.903708835966	0.000535
∞	∞		−2.903724034618	0.0000117

energy $E(\eta)$. The reason is that with the increasing basis set the second derivative of the function $E(\eta)$ in minimum goes to zero, see Ref. 37. Therefore small variations of η around the minimum yield energies that differ negligibly.

It is seen from Table II that convergence of the variational energy levels towards the exact one is rapid at the beginning but rather slow afterwards. It is quite remarkable that we can get "chemical accuracy" -2.903, i.e., error about 1 kcal/mol just with 55 basis functions considering the simplicity of the wave function used. However, it is seen from Table II that to go beyond this "chemical accuracy" it is very difficult. This slow convergence can be partially removed by extrapolating the results for finite basis sets to the infinite one by using the Thiele–Padé extrapolation.[50,62] The result for $n_{12}=40$ is $E(40)=-2.903\,708\,8$ compared to the exact result obtained with the explicitely correlated functions $-2.903\,724\,377$.[8] Extrapolating the values given in the Table II from n_{12} equal to 30 to n_{12} equal to 40 with respect to n_{12}^{-3} we obtained $-2.903\,724\,0$. Extrapolating from the interval $n_{12}=28$ to $n_{12}=38$ we obtained $-2.903\,723\,98$, so reliable part of the extrapolated result is $E_{\mathrm{extr}}=-2.903\,724$. The dependence of $E(n_{12})$ on n_{12}^{-3} was guessed by analyzing the values from $n_{12}=20$ to $n_{12}=40$. It is seen that the extrapolation improves the variational result by two orders.

The slow convergence of the CI method for the ground state of helium is well known and was analyzed in detail in several papers.[38,39,41,42] This slow convergence is related to slow convergence of the multipole expansion for the ground state energy because of the cusp of the wave function for $r_1=r_2$. For this reason the multipole expansion of r_{12}^{-1} has been abandoned in the accurate calculations of two electron atoms and the explicitely correlated functions were introduced. Nevertheless, even for the two-electron atoms the standard CI is more advantegeous than the use of the explicitely correlated functions in the cases when the electron–electron correlation is not so strong. This appears first for the highly ionized two-electron atoms when the interaction between the electrons is supressed by the factor $1/Z$. For such systems, the relativistic and QED effects become very important and it is much easier to calculate the pertinent matrix elements of the

TABLE III. The variational energy levels $E(\eta)$ of the first excited S-state of helium obtained by diagonalization of the generalized eigenvalue problem (27) with the optimized choices of the parameter η. *Order* denotes the order of the truncated matrix. The relative error is calculated with respect to the value -2.1459740292 given in Ref. 64. ∞ denotes the extrapolated value, the extrapolation was made with respect to n_{12}^{-3}.

n_{12}	Order	η	$E(\eta)$	Error $E(\eta)$ [%]
28	1015	0.75446	-2.145962069450	0.000557
29	1120	0.73376	-2.145963231801	0.000503
30	1240	0.71477	-2.145964245885	0.000455
31	1360	0.69624	-2.145965134389	0.000414
32	1496	0.67907	-2.145965916881	0.000378
33	1632	0.66286	-2.145966608567	0.000345
34	1785	0.64685	-2.145967222783	0.000317
35	1938	0.63233	-2.145967769878	0.000291
36	2109	0.61763	-2.145968259173	0.000268
37	2280	0.60442	-2.145968697983	0.000248
38	2470	0.59219	-2.145969092719	0.000230
39	2660	0.57911	-2.145969449151	0.000213
40	2870	0.56765	-2.145969771531	0.000198
∞	∞		-2.145974038455	0.419×10^{-6}

relativistic and QED operators in the basis considered in this paper than in the basis of the explicitely correlated functions. Second, for the excited states, especially for the states with total angular momenta larger than zero, the electron–electron correlation is decreased due to the different angular distribution of the electron orbitals. Intuitively, the electron-electron correlation is the strongest in the case of the S-states and especially for the ground state where the electrons, roughly speaking, occupy the same orbital. From Table III it is seen that already for the first excited S-state the performance of the method is better. It is expected than in the combination with the complex scaling method the performance of the method for higher excited states will further improve.[27]

Finally, let us point out that to judge overall performance of the technique described we should have in mind the last sentences from the Introduction.

VI. CONCLUSIONS

In this paper the use of so(2,1) Lie algebra for calculation of the spectra of the two-electron atoms was suggested. It was shown that by applying this algebra we were able to express all the necessary matrix elements in the analytic form. Particularly, we succeeded in expressing the repulsion integrals in terms of the hypergeometric functions. This was done in three steps, all of them are completely novel from the methodological point of view.

First, we formulated analog of the Wigner–Eckart theorem for so(2,1) algebra. In this way we reduced the repulsion integrals over four radial functions to the repulsion integrals over two radial functions. Second, combining algebraic technique with the integration by parts we derived recurrence relations for the repulsion integrals over two radial functions. Third, we solved the recurrence relations, in form of the difference equations in two variables, in terms of the hypergeometric functions. These *analytic and numerical stable* formulas for the repulsion integrals are the main result of this paper. It solves the problem of the numerical stability and enables us to make the large scale CI calculation with analytic basis functions.

As an illustration, the full CI calculation with increasing basis set for the ground state of helium was made. It is well-known that the electron–electron correlation is in this case very strong. Nevertheless, we showed that by means of the Thiele–Padé extrapolation more accurate results can be obtained. This extrapolation technique is rather straightforward. With more sophisticated technique of extrapolation we can expect even better results. This will be published in the forthcoming paper in which also the methodical problems of extrapolation (including *ab initio* estimate of the error) will be discussed. Our calculation cannot, of course, compete with that obtained by means of the explicitely correlated functions. However, since the numerical difficulties are encountered also within that approach, some of the ideas introduced in this paper could be usefull also in those calculations.

Also, one may expect that the ideas introduced in this paper can be applied to Gaussian functions used in most of quantum chemical calculations.

In this paper we restricted our attention to the calculation of the states with the total square of the angular momentum equal to zero and to the singlet spin states and we used just one screening constant to optimize the energy. However, only slight modifications are necessary to deal also with the states of different symmetry and with more screening constants. These modifications will be discussed in the forthcoming paper.

The method described in this paper can also be used for calculation of $1/Z$ expansion (see, e.g., Refs. 9, 63), the variational and perturbational calculation of atoms with more than two electrons, the inclusion of the relativistic and QED corrections for the two-electron atoms with large Z and the calculation of the dynamical problems on helium like one- and two-photon transitions.[64,65]

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Erratum: "The use of so(2,1) algebra for the evaluation of atomic integrals: The study of two-electron atoms" [J. Math. Phys. 45, 2674 (2004)]

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Equation (43) should read

$$c^{l_i,l_j}_{n_i,n_j,n} = C^{l_i,l_j}_{n_i,n_j,n} - \frac{n_i+n_j-l_i-l_j-2-n}{n_i+n_j+l_i+l_j-n-1} C^{l_i,l_j}_{n_i,n_j,n+1}.$$

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Method of variation of constants for difference equations and its application to the calculation of atomic integrals

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In this paper we extend the method for numerically stable calculation of the atomic integrals suggested in our previous paper for the S-states of two-electron atoms to the states with arbitrary total angular momenta. The extension consists in finding numerically stable forms of the solution of difference equations appearing in the calculation of the radial part of the atomic integrals. These equations become for some value of the independent variable homogenous and their solution in that region is described by one of the two linearly independent solutions. Modification of the method of the variation of constants for this special type of linear second order inhomogenous difference equations is suggested and applied. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1849811]

I. INTRODUCTION

This work grew out from the search for a numerically stable method of the solution of linear inhomogenous second order difference equations appearing in the calculation of the radial part of the atomic integrals.[1] Generally, once we know one of the two linearly independent solutions of the homogenous equation, the second solution can be obtained by the method of the reduction of order.[2] The solution of the inhomogenous equation is then obtained by the method of the variation of constants.[2] However, it turns out that for the difference equations appearing in the calculation of the atomic integrals this general well-known procedure is of little use in its standard form. The reason is that these difference equations become for certain values of the independent variable homogenous and their solution in that region is described by one of the two linearly independent solutions. This behavior results from the general formula by several cancellations of large numbers. If these cancellations are left on the computer working, for example, in double precision arithmetics, totally wrong results are obtained.

Therefore, a general method for obtaining a numerically stable solution of this type of difference equation is given in this paper. The method is applied to the special case of difference equations appearing in the calculation of the radial part of the atomic integrals. Thus, the method suggested in our previous paper for the S-states of the two-electron atoms is extended here to the states with arbitrary total angular momenta. Since in general there are at most two-electron interactions, these results can be extended to all atoms and more generally to all one-center integrals.

The paper is organized as follows. In Sec. II we briefly summarize the calculation of the atomic integrals via the multipole expansion of Coulomb potential. Here, we proceed along the lines of our previous paper.[1] After integrating out angular degrees of freedom, we use analog of the Wigner–Eckart theorem for the radial functions. This reduces the integration over four radial functions to the integration over two radial functions. Then we write down a generalization of the difference equations for the reduced radial integrals derived in Ref. 1 for the S-states to the states of arbitrary total angular momenta of the electrons. The main difference is the fact that for the states of the nonzero total angular momentum the difference equations are inhomogenous. In Sec. III we discuss solutions of these equations. We present results of numerical experiments that show

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that the difference equations are in a region where they are homogenous described by just one of the two linearly independent solutions. In Sec. IV we first briefly summarize general methods of the reduction of order and the variation of constants. We modify the method of the variation of constants for the cases when the second of the two linearly independent solutions of homogenous equations is obtained by the method of the reduction of order. The form proposed by us is more suitable for computational purposes. We then turn our attention to the special type of equations appearing in the calculation of the atomic integrals and derive numerically stable forms of their solution. In Sec. V we apply the general method of Sec. IV to the difference equations for the reduced radial integrals and test it for the case of very large quantum numbers. In Sec. VI, a summary of the achieved results and perspectives of their further applications are given. In the Appendix computationally suitable forms of the hypergeometric functions needed in Secs. II and III are given.

II. CALCULATION OF THE ATOMIC INTEGRALS

In this section we derive the difference equations for the reduced radial part of the atomic integrals. The derivation of these equations was given in great detail in Ref. 1 for the S-states of two-electron atoms. What is difficult in the extension of the method described in Ref. 1 for the S-states to the general state is the *solution* of these difference equations, not their derivation. Therefore, we shall proceed very briefly.

We search for the exact two-electron wave function by the expansion into the symmetry adapted products of the one-electron wave functions

$$|i\rangle = 2^{-(1+\delta_{l_{i1},l_{i2}}\delta_{n_{i1},n_{i2}})/2}[R_{n_{i1},l_{i1}}(r_1)R_{n_{i2},l_{i2}}(r_2)|(l_{i1},l_{i2})L\rangle \pm R_{n_{i2},l_{i2}}(r_1)R_{n_{i1},l_{i1}}(r_2)|(l_{i2},l_{i1})L\rangle]. \tag{1}$$

Here, the states $|(l_1,l_2)L\rangle$ are the eigenfunctions of the square and the third component of the sum of the angular momenta of two electrons

$$|(l_1,l_2)L\rangle = \sum_{m_1=-l_1}^{l_1} (l_1,m_1,l_2,M-m_1|L,M)|l_1,m_1\rangle^{(1)}|l_2,M-m_1\rangle^{(2)}, \tag{2}$$

where $(\,|\,)$ denotes Clebsch–Gordan coefficients. Their explicit form is given, for example, in Refs. 3–5. The radial functions $R_{n,l}$ are eigenfuctions of one of the generators of the so(2,1) algebra[1] and will be described in greater detail later.

A. Multipole expansion

The matrix elements of the Coulomb interaction, i.e., repulsion integrals, are calculated by means of the multipole expansion of the operator r_{12}^{-1},

$$r_{12}^{-1} = \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\vec{n}_1\,.\,\vec{n}_2), \tag{3}$$

where $r_<=\min(r_1,r_2)$ and $r_>=\max(r_1,r_2)$, $P_l(x)$ denotes the Legendre polynomials. With the usual definition of the inner product (to avoid confusion we note that the inner product used in Ref. 1 differs from the usual one by the factor r^{-1}) and multipole expansion (3) the matrix elements of the operator r_{12}^{-1} between the states (1) can be written as

$$\langle i|r_{12}^{-1}|j\rangle = 2^{-(\delta_{n_{i1},n_{i2}}\delta_{l_{i1},l_{i2}}+\delta_{n_{j1},n_{j2}}\delta_{l_{j1},l_{j2}})/2}\left[\sum_{l=\max(|l_{i1}-l_{j1}|,|l_{i2}-l_{j2}|)}^{\min(l_{i1}+l_{j1},l_{i2}+l_{j2})} \theta_{l_{i1},l_{i2},l_{j1},l_{j2},l}X^{l_{i1},l_{i2},l_{j1},l_{j2},l}_{n_{i1},n_{i2},n_{j1},n_{j2}}\right.$$
$$\left.\pm\sum_{l=\max(|l_{i1}-l_{j2}|,|l_{j1}-l_{i2}|)}^{\min(l_{i1}+l_{j2},l_{j1}+l_{i2})} \theta_{l_{i1},l_{i2},l_{j2},l_{j1},l}X^{l_{i1},l_{i2},l_{j2},l_{j1},l}_{n_{i1},n_{i2},n_{j2},n_{j1}}\right], \tag{4}$$

where l in the summation increases by 2.

The angular part $\theta_{l_{i1},l_{i2},l_{j1},l_{j2},l}$ corresponds to the matrix elements of the Legendre polynomials $P_l(\vec{n}_1 . \vec{n}_2)$ between the coupled states (2),

$$\begin{aligned}\theta_{l_{i1},l_{i2},l_{j1},l_{j2},l} &= \langle (l_{i1},l_{i2})L|P_l(\vec{n}_1 . \vec{n}_2)|(l_{j1},l_{j2})L\rangle \\ &= (-1)^{L+l+l_{i1}-l_{j1}+l_{i2}-l_{j2}} \frac{\sqrt{(2l_{i1}+1)(2l_{i2}+1)(2l_{j1}+1)(2l_{j2}+1)}}{2l+1} \\ &\quad \times W(l_{i1},l_{j1},l_{i2},l_{j2},l,L)(l_{i1},0,l_{j1},0|l,0)(l_{i2},0,l_{j2},0|l,0), \end{aligned} \tag{5}$$

where $W(a,b,c,d;e,f)$ are the so-called Racah coefficients and their explicit form is given, for example, in Refs. 4 and 5. The Clebch–Gordan coefficients $(a,0,b,0|c,0)$ are zero unless a, b, and c satisfy the triangle inequality $|a-b| \leqslant c \leqslant a+b$ and $a+b+c$ is even. This reduces the infinite sum in Eq. (3) to the finite number of terms in Eq. (4).

The radial part of the integration reads

$$\begin{aligned} X^{l_{i1},l_{i2},l_{j1},l_{j2},l}_{n_{i1},n_{i2},n_{j1},n_{j2}} &= \int_0^\infty dr_1 \int_0^\infty dr_2\, r_1^2 r_2^2 R_{n_{i1},l_{i1}}(r_1) R_{n_{i2},l_{i2}}(r_2) \frac{r_<^l}{r_>^{l+1}} R_{n_{j1},l_{j1}}(r_1) R_{n_{j2},l_{j2}}(r_2) \\ &= \int_0^\infty dr_1\, R_{n_{i1},l_{i1}}(r_1) R_{n_{j1},l_{j1}}(r_1) r_1^{l+2} \int_{r_1}^\infty dr_2\, R_{n_{i2},l_{i2}}(r_2) R_{n_{j2},l_{j2}}(r_2) r_2^{-l+1} \\ &\quad + \int_0^\infty dr_1\, R_{n_{i1},l_{i1}}(r_1) R_{n_{j1},l_{j1}}(r_1) r_1^{-l+1} \int_0^{r_1} dr_2\, R_{n_{i2},l_{i2}}(r_2) R_{n_{j2},l_{j2}}(r_2) r_2^{l+2}. \end{aligned} \tag{6}$$

B. Reduction of the radial integrals

Using the analog of the Wigner–Eckart theorem for so(2,1) algebra[1] we can write the integrals over four radial functions as a linear combination of the integrals over two radial functions

$$\begin{aligned} X^{l_{i1},l_{i2},l_{j1},l_{j2},l}_{n_{i1},n_{i2},n_{j1},n_{j2}} &= 2^{-2} A^{l_{i1},l_{j1}}_{n_{i1},n_{j1}} A^{l_{i2},l_{j2}}_{n_{i2},n_{j2}} \sum_{n_1=-1}^{n_{i1}+n_{j1}-l_{i1}-l_{j1}-2} c^{l_{i1},l_{j1}}_{n_{i1},n_{j1},n_1} \sum_{n_2=-1}^{n_{i2}+n_{j2}-l_{i2}-l_{j2}-2} c^{l_{i2},l_{j2}}_{n_{i2},n_{j2},n_2} \\ &\quad \times \tilde{Q}^{l_{i1}+l_{j1},l_{i2}+l_{j2},l}_{n_{i1}+n_{j1}-1-n_1,n_{i2}+n_{j2}-1-n_2}, \end{aligned} \tag{7}$$

where the multiplicative factor $A^{l_i,l_j}_{n_i,n_j}$ equals

$$A^{l_i,l_j}_{n_i,n_j} = \frac{2^{1-n_i-n_j}(n_i+n_j-l_i-l_j-2)!(n_i+l_i+n_j+l_j)!}{(n_i-l_i-1)!(n_j-l_j-1)!} \sqrt{\frac{(n_i-l_i-1)!}{(n_i+l_i)!}} \sqrt{\frac{(n_j-l_j-1)!}{(n_j+l_j)!}}. \tag{8}$$

The coefficients $c^{l_i,l_j}_{n_i,n_j,n}$ of the linear combination read

$$c^{l_i,l_j}_{n_i,n_j,n} = C^{l_i,l_j}_{n_i,n_j,n} - \frac{(n_i+n_j-l_i-l_j-2-n)}{(n_i+n_j+l_i+l_j-n-1)} C^{l_i,l_j}_{n_i,n_j,n+1}, \tag{9}$$

where the coefficients $C^{l_i,l_j}_{n_i,n_j,n}$ are given as

$$C^{l_i,l_j}_{n_i,n_j,n} = \frac{F(-n_i+l_i+1,-n;-n_i-n_j+l_i+l_j+2;2)F(-n_i-l_i,-n;-n_i-n_j-l_i-l_j;2)}{(n_i+l_i+n_j+l_j-n-1)!n!} \tag{10}$$

for $n \geqslant 0$ and equal zero otherwise. Here, $F(\alpha,\beta;\gamma;z)$ denotes the hypergeometric function (see, e.g., Refs. 6–8). We note that Eq. (43) in Ref. 1 is incorrect.

$\tilde{Q}^{L_1,L_2,l}_{N_1,N_2}$ denotes the integrals over two radial functions

$$\tilde{Q}^{L_1,L_2,l}_{N_1,N_2} = \tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2} + \tilde{Q}^{-,L_1,L_2,l}_{N_1,N_2}. \tag{11}$$

Here,

$$\tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2} = \int_0^\infty \mathrm{d}r_1\, \tilde{R}_{N_1,L_1}(2r_1) r_1^{l+1} \int_{r_1}^\infty \mathrm{d}r_2\, \tilde{R}_{N_2,L_2}(2r_2) r_2^{-l} \tag{12}$$

and

$$\tilde{Q}^{-,L_1,L_2,l}_{N_1,N_2} = \int_0^\infty \mathrm{d}r_1\, \tilde{R}_{N_1,L_1}(2r_1) r_1^{-l} \int_0^{r_1} \mathrm{d}r_2\, \tilde{R}_{N_2,L_2}(2r_2) r_2^{l+1}, \tag{13}$$

where $\tilde{R}_{N,L}(r)$ differs from $R_{N,L}(r)$ by the normalization factor

$$\tilde{R}_{N,L}(r) = 2\sqrt{\frac{(N+L)!}{(N-L-1)!}} R_{N,L}(r). \tag{14}$$

We note that due to the selection rules for the Clebsch–Gordan coefficients mentioned earlier the difference $|L_1 - L_2|$ is always even. Moreover, the sum $L_1 + L_2 + l$ must be even as well.

C. Difference equations for the reduced integrals

Proceeding in complete analogy with the considerations made in Ref. 1 we obtain the following difference equations for the integrals $\tilde{Q}^{\pm,L_1,L_2,l}_{N_1,N_2}$,

$$(N_2 - L_2)\tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2+1} - (N_2 + L_2)\tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2-1} - 2l\tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2} = -p^{L_1,L_2}_{N_1,N_2} \tag{15}$$

and

$$(N_1 - L_1)\tilde{Q}^{+,L_1,L_2,l}_{N_1+1,N_2} - (N_1 + L_1)\tilde{Q}^{+,L_1,L_2,l}_{N_1-1,N_2} + 2(l+1)\tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2} = p^{L_1,L_2}_{N_1,N_2}. \tag{16}$$

The values of $\tilde{Q}^{-,L_1,L_2,l}_{N_1,N_2}$ are obtained from the relation[1]

$$\tilde{Q}^{-,L_1,L_2,l}_{N_1,N_2} = \tilde{Q}^{+,L_2,L_1,l}_{N_2,N_1}. \tag{17}$$

Here, the right-hand side of equations $p^{L_1,L_2}_{N_1,N_2}$ equals

$$p^{L_1,L_2}_{N_1,N_2} = \int_0^\infty \mathrm{d}r\, r^2 \tilde{R}_{N_1,L_1}(2r)\tilde{R}_{N_2,L_2}(2r). \tag{18}$$

Using the explicit form of the radial functions,[9]

$$\tilde{R}_{n,l}(r) = 2^2 e^{-r}(2r)^l L^{2l+1}_{n-l-1}(2r), \tag{19}$$

and the expression for the generalized Laguerre polynomials (see, e.g., Refs. 6–8)

$$L^{\alpha}_{K}(r) = \frac{1}{K!} e^r r^{-\alpha} \frac{d^K}{\mathrm{d}r^K}(e^{-r} r^{K+\alpha}), \tag{20}$$

we obtain for $L_1 > L_2 + 1$ integrating by parts (see, e.g., Ref. 5),

$$p^{L_1,L_2}_{N_1,N_2} = \frac{(L_1+L_2+2)!}{2} \sum_{q=\max(0,N_2-L_1-2)}^{\min(N_1-L_1-1,N_2-L_2-1)} (-1)^{N_2-L_2-1-q} \times \binom{N_1-L_2-q-3}{L_1-L_2-2}\binom{L_1+L_2+2+q}{L_1+L_2+2}\binom{L_1-L_2+1}{N_2-L_2-1-q} \tag{21}$$

for $N_2 \leq N_1+1$ and

$$p^{L_1,L_2}_{N_1,N_2} = 0 \tag{22}$$

otherwise. The values of $p^{L_1,L_2}_{N_1,N_2}$ for $L_2 > L_1+1$ are obtained from the obvious symmetry $p^{L_1,L_2}_{N_1,N_2} = p^{L_2,L_1}_{N_2,N_1}$, see Eq. (18).

Using difference equations (15) and (16) the integrals are reduced to the integrals over nodeless functions that can be calculated analytically,[1]

$$\tilde{Q}^{+,L_1,L_2,l}_{L_1+1,L_2+1} = 2^{-1}(L_1+L_2+1)!F(1,-L_2+l;-L_1-L_2-1;2). \tag{23}$$

The difference equations (15) and (16) were programmed in MAPLE in form of the recursive algorithm and solved both in rational and 16 digit arithmetics. From these numerical experiments we found that for large quantum numbers N_1, N_2, L_1, and L_2 numerical instabilities appear. Moreover, after some time the recursive algorithm took so much computer memory that further computation was not feasible.

Therefore, we search for the explicit solution of Eqs. (15) and (16). This is done in the following section.

III. SOLUTION OF DIFFERENCE EQUATIONS

In this section we discuss the explicit solution of Eqs. (15) and (16). We argue that the method of variation of constants cannot be used in its standard form and discuss the result of our numerical experiments. These experiments show that Eqs. (15) and (16) are in the region where they are homogenous described by just one of the two linearly independent solutions.

A. The extension of the method given in Ref. 1

In our previous paper[1] we solved Eqs. (15) and (16) for the S-states. It follows from the properties of the Clebsch–Gordan coefficients that we must consider the only case $L_1=L_2=L$. In such a case the situation is simplified by virtue of the fact that the right-hand side $p^{L,L}_{N_1,N_2}$ vanishes whenever $|N_1-N_2|>1$.[1] That means that Eqs. (15) and (16) are for most of the values N_1 and N_2 homogenous. Therefore, it was sufficient to find two linearly independent solutions (fundamental system) of homogenous equations (15) and (16) for $l<L$. The two linearly independent solutions of homogenous equation (15) are

$$a_{N_2} = (-1)^{N_2-L_2-1}F(N_2-L_2,-L_2+l;-2L_2;2) \tag{24}$$

and

$$b_{N_2} = F(N_2-L_2,-L_2-l;-2L_2;2). \tag{25}$$

The two linearly independent solutions of the homogenous equation (16) are

$$a_{N_1} = F(N_1-L_1-1,-L_1+l+1;-2L_1;2) \tag{26}$$

and

$$b_{N_1} = (-1)^{N_1-L_1-1} F(N_1 - L_1, -L_1 - l - 1; -2L_1, 2). \tag{27}$$

For $l=L$, behavior of Eqs. (15) and (16) was so simple that it was possible to guess the result directly from the numerical analysis.

The task of solving Eqs. (15) and (16) is therefore twofold.

First, to determine two linearly independent solutions of homogenous equations (15) and (16) in the cases when $l=\min(L_1,L_2)$. In these cases solutions are not hypergeometric functions. In the Appendix we give a method for finding the solution of Eqs. (15) and (16) in terms of the power series in N_1 or N_2. For $l<\min(L_1,L_2)$ we obtain in this way an alternative expression for the hypergeometric functions. For $l=\min(L_1,L_2)$ this method yields at least one of the two linearly independent solutions. The second solution is found by the method of the reduction of order described in Sec. IV A below.

Second, the fundamental system is used for the solution of inhomogenous equations by the method of the variation of constants. One possibility is to apply this method to Eq. (16) and fix constants on the values $\tilde{Q}^{+,L_1,L_2,l}_{L_1+1,N_2}$ and $\tilde{Q}^{+,L_1,L_2,l}_{L_1+2,N_2}$. Then we apply the method first to Eq. (15) for $N_1=L_1+1$ and fix constants on the values of $\tilde{Q}^{+,L_1,L_2,l}_{L_1+1,L_2+1}$ and $\tilde{Q}^{+,L_1,L_2,l}_{L_1+1,L_2+2}$. Second, we apply the method to Eq. (16) for $N_1=L_1+2$ and fix constants on the values of $\tilde{Q}^{+,L_1,L_2,l}_{L_1+2,L_2+1}$ and $\tilde{Q}^{+,L_1,L_2,l}_{L_1+2,L_2+2}$. Such solution, however, is neither fast nor numerically stable. The reason is that solution of Eqs. (15) and (16) is simplified by virtue of the fact that these equations become homogenous for $L_1<L_2$ and $N_1>N_2+1$ or $L_1>L_2$ and $N_2>N_1+1$, see Eq. (22). Further simplifications were found from numerical experiments given below. All these simplifications must be carefully examined and taken into account to get numerically stable formulas.

B. Numerical experiments

We found that Eq. (15) can be for $L_1>L_2$ and $N_2>N_1+1$ described by just one of the two linearly independent solutions,

$$Q^{+,L_1,L_2,l}_{N_1,N_2} = K(N_1,L_1,L_2,l)\,a_{N_2}, \tag{28}$$

where a_{N_2} is given by Eq. (24). This equation holds for $l<L_2$. For $l=L_2$ the dependence of $Q^{+,L_1,L_2,L_2}_{N_1,N_2}$ on N_2 can be described as

$$Q^{+,L_1,L_2,L_2}_{N_1,N_2} = K(N_1,L_1,L_2)(-1)^{N_2-L_2-1}. \tag{29}$$

Equation (16) behaves in the same way for $L_2>L_1$ and $N_1>N_2+1$,

$$Q^{+,L_1,L_2,l}_{N_1,N_2} = K(N_2,L_1,L_2,l)\,a_{N_1}, \tag{30}$$

where a_{N_1} is given by Eq. (26). This equation holds for $l<L_1$. For $l=L_1$ and $N_1>N_2$ we found

$$Q^{+,L_1,L_2,L_1}_{N_1,N_2} = 0. \tag{31}$$

These results show that Eq. (15) is for $L_1>L_2$ and $N_2>N_1+1$ described by just *one* of the two linearly independent solutions. Equation (16) behaves in this way for $L_1<L_2$ and $N_1>N_2+1$. A consequence of this is that although Eqs. (15) and (16) are three term recursion relations we need in the case of Eq. (15) for $L_1>L_2$ and in the case of Eq. (16) for $L_1<L_2$ just *one* initial condition instead of two. In the case of Eq. (16) for $L_1<L_2$ and $l=L_1$ we do not need initial conditions at all. From numerical experiments given in Sec. V below, we were able to determine these initial conditions, that means to determine behavior of $\tilde{Q}^{+,L_1,L_2,l}_{N_1,L_2+1}$ for $L_1>L_2$ and $\tilde{Q}^{+,L_1,L_2,l}_{L_1+1,N_2}$ for $L_1<L_2$ and $l<L_1$.

This simplifies the situation tremendously because it means that *instead of solving both Eqs. (16) and (15) simultaneously, we must solve only Eq. (16) for* $L_1<L_2$ *and Eq. (15) for* $L_1>L_2$.

As it is clear from the above discussion we need modification of the method of the variation of constants for the case when one of the solutions is obtained by the method of the reduction of order [the case $l=\min(L_1,L_2)$] and for special types of equations when for some value of independent variable equations become homogenous and their solution in that region is described by one of the two linearly independent solutions [Eq. (16) for $L_1<L_2$ and Eq. (15) for $L_1>L_2$]. A general theory of the variation of constants for these cases is given in the following section.

IV. GENERAL THEORY

In this section a general modification of the method of variation of constants is described. We consider general linear second order inhomogenous difference equations for the discrete function f_n,

$$f_{n+1}+q_nf_n+r_nf_{n-1}=s_n. \tag{32}$$

We assume that $f_n=0$ for $n<L+1$ where L is integer and that $s_n=0$ for all $n>M+1$. Equation (15) is obtained from this general equation by setting $n=N_2$, $L=L_2$, $M=N_1$, and $f_{N_2}=\tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2}$. Equation (16) is obtained from this general equation by setting $n=N_1$, $L=L_1$, $M=N_2$, and $f_{N_1}=\tilde{Q}^{+,L_1,L_2,l}_{N_1,N_2}$. With these assignments we have for both cases

$$r_n=-\frac{n+L}{n-L}. \tag{33}$$

We first show the method of the reduction of order. This is not new, but for the sake of further considerations we describe it in greater detail. Then we summarize the method of the variation of constants and modify it for the cases when one of the solutions was obtained by the reduction of order and for special types of equations appearing in the calculation of atomic integrals.

A. Reduction of order

Let a_n be a solution of the homogenous equation

$$a_{n+1}+q_na_n+r_na_{n-1}=0. \tag{34}$$

The second linearly independent solution can be found by the method of the reduction of order. We search for it in the form

$$b_n=(x_n-x_L)a_n. \tag{35}$$

Inserting it into homogenous equation (32) (with $s_n=0$) and using Eq. (34) we obtain after some manipulation

$$d_{n+1}=r_n\frac{a_{n-1}}{a_{n+1}}d_n, \tag{36}$$

where

$$d_n=x_n-x_{n-1}. \tag{37}$$

Considering the last equation successively for descending n we get

$$x_j-x_n=\sum_{i=n+1}^{j}d_i. \tag{38}$$

Considering Eq. (36) successively for descending n we get

$$d_n = \prod_{k=n-m}^{n-1} r_k \frac{a_{n-m}a_{n-m-1}}{a_n a_{n-1}} d_{n-m}. \tag{39}$$

Since $a_n=0$ for $n<L+1$ we set $n-m-1=L+1$ in the last equation. Then we obtain for d_n,

$$d_n = \frac{\prod_{k=L+2}^{n-1} r_k}{a_n a_{n-1}} a_{L+2}a_{L+1}d_{L+2}. \tag{40}$$

Inserting this equation into Eq. (38) we get finally

$$x_j - x_n = a_{L+2}a_{L+1}d_{L+2} \sum_{i=n+1}^{j} \frac{\prod_{k=L+2}^{i-1} r_k}{a_i a_{i-1}}. \tag{41}$$

B. Variation of constants

Having two linearly independent solutions a_n and b_n of the homogenous equation a general solution of the inhomogenous equation (32) is obtained by the method of variation of constants[2]

$$f_n = c_1 a_n + c_2 b_n + \sum_{j=L+2}^{n-1} T_j(b_j a_n - a_j b_n). \tag{42}$$

Here, T_j denotes the ratio

$$T_j = \frac{s_j}{W_j}, \tag{43}$$

where W_j is the Wronskian of the solutions

$$W_j = a_{j+1}b_j - a_j b_{j+1}. \tag{44}$$

The constants c_1 and c_2 in Eq. (42) are fixed by the initial values f_{L+1} and f_{L+2}.

For further considerations we derive an alternative form of the Wronskian W_j, see also Ref. 2. Inserting b_j from Eq. (35) we rewrite Eq. (44) into the form

$$W_j = -a_{j+1}a_j(x_{j+1} - x_j). \tag{45}$$

Inserting the difference $x_{j+1}-x_j$ from Eq. (41) into the last equation we obtain

$$W_j = -a_{L+2}a_{L+1}d_{L+2} \prod_{k=L+2}^{j} r_k. \tag{46}$$

Since

$$W_{L+1} = -a_{L+2}a_{L+1}d_{L+2} \tag{47}$$

we can write

$$W_j = W_{L+1} \prod_{k=L+2}^{j} r_k. \tag{48}$$

By means of Eq. (47) we can rewrite also Eq. (41) into the form

$$x_j - x_n = - W_{L+1} \sum_{i=n+1}^{j} \frac{\prod_{k=L+2}^{i-1} r_k}{a_i a_{i-1}}. \tag{49}$$

We note that, quite generally, formula (42) can be set into an alternative form. Inserting b_n from Eq. (35) we get

$$f_n = a_n[c_1 + c_2(x_n - x_L) + \sum_{j=L+2}^{n-1} T_j a_j (x_j - x_n)], \tag{50}$$

where the difference $x_j - x_n$ is given by Eq. (49). This form of the solution is likely to be less numerically unstable than the form (42), especially in the cases where one of the solutions was obtained by the method of the reduction of order. The reason is that in Eq. (42) we subtract the numbers $b_j a_n$ and $a_j b_n$. Inserting b_j from Eq. (35) we see that we subtract in fact $a_j a_n (x_j - x_L)$ and $a_j a_n (x_n - x_L)$. These two numbers can be very large especially for large n and j. Therefore their subtraction can cause a loss of significant digits. The advantage of Eq. (50) is that we directly calculate the *result* of the subtraction.

C. Special type of equations

Until now, our considerations were quite general. Now we turn to the special type of Eq. (32) for which $s_n = 0$ for all $n > M+1$ where M is integer and the solution of Eq. (32) in this region is fully described by just *one* of the two linearly independent solutions of the homogenous equation

$$f_n = K a_n, \tag{51}$$

where K is independent on n. Comparing Eqs. (50) and (51) we get

$$K = c_1 + (x_n - x_L) c_2 + \sum_{j=L+2}^{M+1} T_j a_j (x_j - x_n) \tag{52}$$

for arbitrary $n > M+1$. Since this equation holds for $n > M+1$ independently on the value of n we get

$$c_1 - x_L c_2 + \sum_{j=L+2}^{M+1} T_j a_j x_j = K \tag{53}$$

and

$$c_2 - \sum_{j=L+2}^{M+1} T_j a_j = 0. \tag{54}$$

The last two equations are a source of numerical instabilities if constants c_1 and c_2 are determined from the initial values f_{L+1} and f_{L+2}. To avoid these instabilities *we use Eqs. (53) and (54) as equations determining constants* c_1 *and* c_2. If we do so and insert the result into Eq. (50) we obtain

$$f_n = a_n \left[K - \sum_{j=n}^{M+1} T_j a_j (x_j - x_n) \right]. \tag{55}$$

Considering this equation for $n = L+1$ we determine the constant K,

$$K=\frac{f_{L+1}}{a_{L+1}}+\sum_{j=L+1}^{M+1}T_ja_j(x_j-x_{L+1}). \tag{56}$$

Inserting this back into Eq. (55) we obtain finally

$$f_n=a_n\left[\frac{f_{L+1}}{a_{L+1}}+\sum_{j=L+2}^{n-1}T_ja_j(x_j-x_{L+1})+\sum_{j=n}^{M+1}T_ja_j(x_n-x_{L+1})\right]. \tag{57}$$

Alternatively, we can use Eq. (35) and rewrite Eq. (57) in terms of a_n and b_n,

$$f_n=\frac{a_n}{a_{L+1}}\left[f_{L+1}-\sum_{j=L+2}^{M+1}T_ja_jb_{L+1}\right]+a_n\sum_{j=L+2}^{n-1}T_jb_j+b_n\sum_{j=n}^{M+1}T_ja_j. \tag{58}$$

The last two equations are likely to be more convenient for computational purposes than Eq. (42) since there are no cancellations of large numbers in these equations. The possible exception is the subtraction in the square brackets in Eq. (58), but for the special case of interest (see Sec. V) we avoid this difficulty.

V. APPLICATION OF THE METHOD

General theory outlined in the preceding section will be applied to the difference equations (15) and (16). To do so, we need to calculate T_j from Eq. (43).

A. Calculation of T_j

First we calculate Wronskian (44) from Eq. (48). Inserting r_k from Eq. (33) into this equation we get that Wronskian behaves for both Eqs. (15) and (16) as

$$W_j=(-1)^{j-L-1}\frac{(j+L)!}{(j-L)!}\frac{W_{L+1}}{(2L+1)!}, \tag{59}$$

where we set either $L=L_2$ or $L=L_1$. We note that W_{L+1} is the only quantity in this equation that depends on the concrete form of a_j and b_j.

Second, we take the right-hand side s_j of Eq. (32) equal to

$$s_j=-\frac{p_{N_1,j}^{L_1,L_2}}{j-L_2} \tag{60}$$

in case of Eq. (15) and

$$s_j=\frac{p_{N_2,j}^{L_2,L_1}}{j-L_1} \tag{61}$$

in case of Eq. (16).

Equations (59), (60), and (61) can be used to simplify formula (43). By inserting Eq. (59) with $L=L_2$ and Eq. (60) into Eq. (43) we get in the case of Eq. (15),

$$T_j=-\frac{p_{N_1,j}^{L_1,L_2}}{W_{L_2+1}}. \tag{62}$$

Analogously, by inserting Eq. (59) with $L=L_1$ and Eq. (61) into Eq. (43) we get in the case of Eq. (16),

$$T_j = \frac{P^{L_2,L_1}_{N_2,j}}{W_{L_1+1}}. \tag{63}$$

Here, $P^{L_1,L_2}_{N_1,N_2}$ denotes

$$P^{L_1,L_2}_{N_1,N_2} = \frac{p^{L_1,L_2}_{N_1,N_2} W_{L_2+1}}{(N_2 - L_2) W_{N_2}}. \tag{64}$$

This quantity was introduced because of the symmetry

$$P^{L_1,L_2}_{N_1,N_2} = P^{L_2,L_1}_{N_2,N_1} \tag{65}$$

[see the notes after Eqs. (22) and (59)]. By combining Eqs. (21) and (59) we can write for $L_1 > L_2 + 1$,

$$P^{L_1,L_2}_{N_1,N_2} = \frac{(L_1 - L_2 + 1)!(2L_2 + 1)!}{2} \sum_{q=\max(0,N_2-L_1-2)}^{\min(N_1-L_1-1,N_2-L_2-1)} (-1)^q \times \binom{N_1 - L_2 - q - 3}{L_1 - L_2 - 2} \binom{N_2 - L_2 - 1}{q} \binom{L_1 + L_2 + 2 + q}{N_2 + L_2}. \tag{66}$$

The case $L_2 > L_1 + 1$ is calculated by means of Eq. (65).

B. Numerical experiments and final formulas

1. Case $l < \min(L_1, L_2)$

By numerical experiments we found that the initial values f_{L+1} for Eq. (15) with $L_1 > L_2$ and $l < L_2$ and for Eq. (16) with $L_1 < L_2$ and $l < L_1$ are given as

$$f_{L+1} = (a_{L+1} + b_{L+1}) \sum_{j=L+1}^{M+1} T_j a_j. \tag{67}$$

In the case of Eq. (15) this equation holds with $L = L_2$, $M = N_1$, $f_{L+1} = \tilde{Q}^{+,L_1,L_2,l}_{N_1,L_2+1}$ and with a_j, b_j, and T_j given by Eqs. (24), (25), and (62). In the case of Eq. (16) this equation holds with $L = L_1$, $M = N_2$, $f_{L+1} = \tilde{Q}^{+,L_1,L_2,l}_{L_1+1,N_2}$ and with a_j, b_j, and T_j given by Eqs. (26), (27), and (63).

Then Eq. (58) can be brought to the form

$$f_n = a_n \sum_{j=L+1}^{n-1} T_j (a_j + b_j) + (a_n + b_n) \sum_{j=n}^{M+1} T_j a_j. \tag{68}$$

2. Case $l = L_2$

It follows from Eq. (29) that in this case one of the two linearly independent solutions is

$$a_{N_2} = (-1)^{N_2 - L_2 - 1}. \tag{69}$$

The second one is determined by the reduction of order. We use Eq. (57) for $f_{N_2} = \tilde{Q}^{+,L_1,L_2,L_2}_{N_1,N_2}$ with $n = N_2$, $L = L_2$, $M = N_1$, and T_j given by Eq. (62). The value of f_{L+1} was found from numerical analysis to be

$$\tilde{Q}^{+,L_1,L_2,L_2}_{N_1,L_2+1} = \frac{(L_1 + L_2 + 1)!(N_1 - L_2 - 2)!}{2(L_1 - L_2 - 1)!(N_1 - L_1 - 1)!}. \tag{70}$$

3. Case $l=L_1$

It follows from Eq. (31) that the constant K in Eq. (51) is equal to zero, so we can use Eq. (55) for $f_{N_1}=\tilde{Q}^{+,L_1,L_2,L_1}_{N_1,N_2}$ with $n=N_1$, $L=L_1$, $M=N_2$, and T_j calculated from Eq. (63).

One of the two linearly independent solutions of homogenous equation (16) is given by Eq. (A6) of the Appendix with $J=2L_1+1$,

$$a_{N_1}=(-1)^{N_1-L_1-1}\sum_{j=0}^{2L_1+1} h_j(N_1-L_1)^j, \tag{71}$$

where h_j are given by Eq. (A11) and where $h_{2L_1+1}=1$.

Using Eqs. (33) and (49) we can write Eq. (55) for the case considered as

$$f_n=-a_n\frac{W_{L+1}}{(2L+1)!}\sum_{j=n+1}^{M+1} T_j a_j \sum_{k=n+1}^{j} \frac{(-1)^{k-L-1}(k+L-1)!}{a_k a_{k-1}(k-L-1)!}. \tag{72}$$

This expression is still not entirely satisfactory. We found that there is residual instability for n close to $L+1$. To eliminate it we rewrite the double summation in the last equation

$$f_n=-a_n\frac{W_{L+1}}{(2L+1)!}\sum_{k=n+1}^{M+1} \frac{(-1)^{k-L-1}(k+L-1)!}{a_k a_{k-1}(k-L-1)!}\sum_{j=k}^{M+1} T_j a_j. \tag{73}$$

The source of instability for n close to $L+1$ is an interesting identity,

$$\sum_{j=L+1}^{M+1} T_j a_j = 0. \tag{74}$$

Therefore, we use this identity in Eq. (73) and rewrite this equation to the form

$$f_n=a_n\frac{W_{L+1}}{(2L+1)!}\sum_{k=n+1}^{M+1} \frac{(-1)^{k-L-1}(k+L-1)!}{a_k a_{k-1}(k-L-1)!}\sum_{j=L+1}^{k-1} T_j a_j. \tag{75}$$

This equation is stable for all n from $L+1$ to M. For $n>M$, it yields zero as it should.

C. Numerical tests

We tested derived formulas numerically for very large quantum numbers. First we set $L_1=16$ and $L_2=14$, second we considered $L_1=20$ and $L_2=10$. We took $N_1=50$ and varied N_2 from L_2+1 to 70 and l from 2 to L_2. Then we reversed the role of L_1 and L_2 and also N_1 and N_2. These tests are rather severe; in normal calculation one encounters much more favorable situations. The formulas were run in double precision arithmetics and compared with the exact solutions of Eqs. (15) and (16) programmed in MAPLE in the form of the recursive algorithm run in rational arithmetics. For $l<\min(L_1,L_2)$, the hypergeometric functions (24)–(27) were calculated from the MAPLE subroutine. The numerical stable way of their calculations is given in the Appendix. For $|L_1-L_2|=2$ the relative error of the derived formulas was typically of order 10^{-15}. For the case $|L_1-L_2|=10$ the relative error was typically two orders higher. This shows that numerical stability of formulas slightly deteriorates with increasing difference $|L_1-L_2|$. However, one can expect that with increasing difference of the angular momenta of the electrons the contributions of the terms with large numbers of nodes to the energy is relatively small. Therefore, the achieved numerical stability is sufficient for all practical purposes.

VI. CONCLUSIONS

In this paper we extended the method of numerically stable calculation of the atomic integrals suggested in our previous paper[1] for the S-states of two-electron atoms to the states of arbitrary total angular momenta. Thus, in these two papers the complete solution of the numerically stable calculation of the atomic integrals is given. In the first paper[1] we succeeded in transformation of the problem of the numerical stable calculation of the atomic integrals to the problem of the numerical stable solution of the difference equations. In this paper we completed our program by solving the latter problem in required generality. To achieve this aim we suggested a computationally stable method for the solution of inhomogenous difference equations that for certain values of the discrete independent variable become homogenous and in that region are described by just one of the two linearly independent solutions. The method was applied to the difference equations appearing in the radial part of the atomic integrals and tested for very large quantum numbers. These tests show high numerical stability of the suggested method. The stability slightly decreases with increasing difference of the angular momenta of the electrons.

The method suggested in these two papers can be used for the calculation of the radial part of the Coulomb interaction between electrons whose orbitals are expanded from the same center. This covers all atoms and the simplest molecules. The results obtained in these papers can be directly used for the configuration interaction calculation of the excited states of two electron atoms. This will be reported elsewhere.

Because of the potential importance of the achieved results it would be desirable to put them on a rigorous basis. The paper is based on the observation that Eqs. (15) and (16) can be in the region where they become homogenous described by just *one* of the two linearly independent solutions. Although we are certain about this observation, one should see *why* equations behave in this way. The same applies to our guesses (67), (70), and (74), and for Eq. (A17) in the Appendix.

Therefore, we believe that the results achieved in this paper are of some interest from the point of view of atomic physics as well as pure mathematics.

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APPENDIX

In this appendix we suggest a solution of the homogenous equations (15) and (16). Since this solution is given in terms of the hypergeometric function $F(a,b,c,2)$ we find a particularly useful form of these functions that can be used also in Eq. (10).

Let us rewrite homogenous equations (15) and (16) into a general form,

$$(n-L)g_{n+1}-(n+L)g_{n-1}-2(J-L)g_n=0. \tag{A1}$$

This equation is obtained from the original homogenous equation (16),

$$(n-L)f_{n+1}-(n+L)f_{n-1}+2(l+1)f_n=0, \tag{A2}$$

by setting either $f_n=g_n$ and $J=L-l-1$ or $f_n=(-1)^n g_n$ and $J=L+l+1$. Equation (A1) is obtained also from homogenous equation (15),

$$(n-L)f_{n+1}-(n+L)f_{n-1}-2lf_n=0, \tag{A3}$$

by setting either $f_n=g_n$ and $J=L+l$ or $f_n=(-1)^n g_n$ and $J=L-l$. Due to the selection rules for Clebsch–Gordan coefficients mentioned after Eq. (5), the difference $L-l$ is always even. Therefore, the parameter J is odd in the case of Eq. (16) and even in the case of Eq. (15).

For $J<L-1$ the solution of Eq. (A1) is given by the hypergeometric function

$$g_n=F(n-L,-J;-2L;2). \tag{A4}$$

Let us remind the form of the hypergeometric function $F(a,b,c,z)$ here,

$$F(a,b,c,z) = 1 + \frac{ab}{c}z + \frac{a(a+1)b(b+1)}{c(c+1)}\frac{z^2}{2!} + \cdots . \tag{A5}$$

It turns out that this form of the hypergeometric functions is useful only for a close to zero, i.e., only for n close to L. For larger n, a more suitable form is needed.

Since we want to get expression also for the hypergeometric functions appearing in Eq. (10), we allow L to be half-integral and n to be half-integral and smaller than $L+1$.

We search for the solution of Eq. (A1) in the form of the series

$$g_n = \sum_{j=0}^{J} h_j (n-L)^j . \tag{A6}$$

Later on, it will be clear why we choose the upper bound of summation J. The advantage of this expansion is that the coefficients h_j do not change the sign. Therefore, for n larger than L this way of calculating the hypergeometric functions is numerically stable and can be used for the hypergeometric functions appearing in Eqs. (24)–(27).

Since J must be a non-negative integer, for $L=l$ we obtain only one solution in the form (A6). If $l<L$, we obtain in this way two linearly independent solutions.

The remaining hypergeometric functions to be calculated are those appearing in Eq. (10). For these functions argument a in the definition (A5) is always negative. As it is clear from Eq. (A4) it corresponds to the situation when $n<L$. The use of Eq. (A6) is not advantageous in this case, because for negative value of $n-L$ we get in (A6) the sum of terms with changing signs. When n is close to L, the best way is to calculate the hypergeometric functions from the definition (A5). For n more distant from L we calculate the hypergeometric functions from the series

$$g_n = \sum_{j=0}^{J} c_j n^j . \tag{A7}$$

It appears that for even J the coefficients c_j with odd j equal zero and for odd J the coefficients c_j with even j equal zero. From this fact it immediately follows that

$$F(-n-L,-J;-2L;2) = (-1)^J F(n-L,-J;-2L,2) . \tag{A8}$$

Using this equation we can always raise the value of the parameter a over $-L$.

In the following we first show how to calculate the coefficients h_j in the expansion (A6), then we calculate the coefficients c_j in the expansion (A7).

Expansion around $n=L$

We make substitution $N=n-L$ in Eq. (A1). Then Eq. (A1) reads

$$N g_{N+1} - (N+2L) g_{N-1} - 2(J-L) g_N = 0. \tag{A9}$$

Inserting the expansion (A6) and using the binomial formula we obtain after some manipulation

$$\sum_{j=0}^{J} \left[\sum_{k=0}^{j} \binom{j}{k} N^{k+1}(1-(-1)^{j-k}) - 2L \sum_{k=0}^{j} N^k (-1)^{j-k} - 2(J-L) N^j \right] h_j = 0. \tag{A10}$$

Comparing now terms with the same powers of N we get for the highest power N^J identically zero. It means that the coefficient h_J is free for the normalization of the solution. This is the reason why we chose in Eq. (A6) the upper bound of the summation equal to J. Going then successively to the lower powers of N we obtain recurrence relations for the coefficients h_j,

$$\frac{h_{J-j}}{h_J} = \frac{1}{j(J-j)!}\sum_{p=0}^{j-1} \frac{(J-p)!}{(1+j-p)!}\left[\frac{1-(-1)^{j-p-1}}{2}(J-j) - L(1+j-p)(-1)^{j-p}\right]\frac{h_{J-p}}{h_J}. \quad \text{(A11)}$$

Normalization of the series (A6) to the hypergeometric function is done by comparing Eqs. (A4) and (A6) for some value of n. The best choice is $n=L$ since then we have

$$1 = h_J\frac{h_0}{h_J}, \quad \text{(A12)}$$

where we used the identity $F(0,-J;-2L;2)=1$. The ratio h_0/h_J is calculated from Eq. (A11).

Expansion around $n=0$

We proceed along the same lines as in the derivation of recurrence relations for the coefficients h_j. We insert the expansion (A7) into Eq. (A1), use binomial formula and compare the terms with the same powers of n. After some manipulation we obtain

$$\frac{c_{J-2p}}{c_J} = \frac{1}{2p(J-2p)!}\sum_{j=0}^{p-1} \frac{c_{J-2j}}{c_J}\frac{(J-2j)!}{(2p-2j+1)!}[J-2p-L(2p-2j+1)] \quad \text{(A13)}$$

for p running from 1 to $J/2$ for J even and to $(J-1)/2$ for J odd. The coefficients c_{J-2p-1} equal zero.

The coefficient c_J is determined by comparing series (A7) and the hypergeometric function (A4) for some n. Setting $n=L$ we obtain

$$1 = c_J\sum_{j=0}^{J} \frac{c_j}{c_J}L^j, \quad \text{(A14)}$$

where we used the identity $F(0,-J;-2L;2)=1$. For practical purposes, however, this form is not very convenient, since there is a cancellation of large numbers in the sum on the right-hand side. For this reason the use of series (A7) is not suitable for calculation of the hypergeometric functions with n comparable or greater than L. Instead we determine the constant c_J as follows.

For even values of $J=2P$ the constant c_{2P} is found by comparing Eqs. (A4) and (A7) for $n=0$,

$$F(-L,-2P;-2L;2) = c_{2P}\frac{c_0}{c_{2P}}, \quad \text{(A15)}$$

where the ratio c_0/c_{2P} is calculated from Eq. (A13). The values of $F(-L,-2P;-2L,2)$ were found from the numerical experiments to be

$$F(-L,-2P,-2L,2) = \prod_{p=0}^{P-1} \frac{2p+1}{2L-2p-1}. \quad \text{(A16)}$$

For odd values of $J=2P+1$, comparison of Eqs. (A4) and (A7) yields for $n=0$ nothing, since both sides are identically equal to zero. However, the constant c_{2P+1} can be calculated from remarkable identity

$$c_{2P+1} = \frac{c_{2P}}{L-P} \quad \text{(A17)}$$

found by numerical experiments.

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Calculation of atomic integrals using commutation relations

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In this paper, a numerically stable method of calculating atomic integrals is suggested. The commutation relations among the components of the angular momentum and the Runge-Lenz vector are used to deduce recurrence relations for the Sturmian radial functions. The radial part of the one- and two-electron integrals is evaluated by means of these recurrence relations. The product of two radial functions is written as a linear combination of the radial functions. This enables us to write the integrals over four radial functions as a linear combination of the integrals over two radial functions. The recurrence relations for the functions are used to derive the recursion relations for the coefficients of the linear combination and for the integrals over two functions.

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I. INTRODUCTION

This paper is concerned with the calculation of atomic wave functions and atomic integrals in an algebraic way. This algebraic approach compares favorably with the analytical one. The algebraic approach enables us to handle the numerical instabilities encountered when calculating atomic integrals. There is also an inherent elegance in this approach.

The accuracy of the spectroscopic measurements achieved such a level that parity violating effects of the weak interactions on the atomic spectra can be measured. For a review of these exciting developments see, e.g., Refs. [1,2]. Together with the corresponding theoretical calculations, see, e.g., Ref. [3], this provides bounds on the mass of new neutral bosons predicted by extensions of the standard model. These bounds are tighter than those achieved in the present collider experiments [3]. Undoubtedly, the search for effects of the physics beyond the standard model on the atomic spectra will continue. More accurate measurements and calculations will be made. In this connection we would like to draw attention to the fact that there is an obstacle in further improvement of the theoretical calculations.

Let us restrict our discussion to the cases when the motion of electrons can be treated in the first approximation as nonrelativistic. Only slight modifications of the following discussion are needed to treat the cases when relativity has to be taken into account from the very beginning. The most accurate approximate method for solution of the Schrödinger equation for many-electron atoms is the method of configuration interaction (CI). It consists of expanding the exact wave function into the antisymmetrized products of one-electron spin orbitals. The orbital component of the spin orbitals is the product of the radial and angular parts.

The CI method can be systematically improved by enlarging the set of one-electron spin orbitals. However, in doing so the following difficulty is encountered. If we consider the orthogonal set of one-electron spin orbitals, we have to include the spin orbitals with radial functions having large number of nodes into the set. These functions change their sign frequently. Calculation of the matrix elements of the Coulomb interaction between these functions in finite precision arithmetics corresponds, from numerical point of view, to the subtraction of two infinities. If we consider nonorthogonal basis set, then we just shift the problem of numerical instabilities from the calculation of the integrals to the diagonalization of Hamiltonian matrix. So far the numerical instabilities have not been analyzed in a systematic way. Thus, they are not controlled. The difficulty caused by numerical instabilities is evident when observing the published numerical calculations.

The form of one-electron spin orbitals is in principle arbitrary. However, to achieve rapid convergence of the CI method, the Sturmian basis set is usually applied, see, e.g., Refs. [4–8]. This set is obtained from hydrogenic basis set via energy-dependent scaling transformation. The solution of the Schrödinger equation for the hydrogen atom is found to be a product of radial and angular functions. The difference in dealing with radial and angular functions is striking. The angular functions are found from commutation relations of so(3) algebra. This enables one to transform the angular integrations of complicated expressions to manageable algebraic manipulations [9–11]. On the other hand, the radial functions are not found from symmetry considerations but as solutions of differential equation. However, this leads to much less manageable numerical instabilities in the radial part of the integration mentioned above.

This observation is the chief motivation for the search of the algebraic treatment of the radial functions presented in this paper. This algebraic treatment is facilitated by high symmetry of the hydrogen atom. There are six operators commuting with hydrogenic Hamiltonian when neglecting spin. They consist of components of angular momentum and components of the Runge-Lenz vector. This vector is integral of motion also in the classical theory. This is a direct consequence of the fact that the classical orbit in Coulomb potential is a conic section. The Runge-Lenz vector has the direction of the principal axis of the conic section. Its magnitude equals to the eccentricity of the conic section, see, e.g., Ref. [12]. These six operators do not mutually commute. However, they are closed under commutation and form so(4) algebra. In addition, there are three radial operators closed under commutation that form so(2,1) algebra. After the energy-dependent scaling transformation so(4) algebra can be merged with so(2,1) algebra into so(4,2) algebra, see, e.g., Ref. [13].

The commutation of the Runge-Lenz vector with hydrogenic Hamiltonian was realized by Pauli even before the discovery of the Schrödinger equation. It was further elaborated by Fock and Bargmann (for an English translation of the original papers see Ref. [14]). Despite the fact that this high symmetry of the hydrogen atom has been known for such a long time it was seldom applied to more complicated atoms. Particularly, Herrick and Sinanoglu applied it to the classification of the doubly excited states of two-electron atoms [15]. Further, de Prunele applied it to the evaluation of the matrix elements of Coulomb interaction in the basis used by Herrick and Sinanoglu [16].

The first aim of this paper is to explore the high symmetry of the hydrogen atom and to relate it to the properties of radial functions. So far, only partial symmetry has been utilized via so(2,1) algebra of radial operators [13,17]. This provided the recurrence relations for radial functions with different principal number n but with the same orbital number l. The ultimate goal is to examine if so(4) algebra relates radial functions with different orbital numbers l. The second aim of this paper is to show that these relations for the radial functions can be used to numerically stabilize the calculation of the matrix elements of Coulomb interaction.

The paper is organized as follows. In Sec. II the energy spectrum of the hydrogen atom and the recurrence relations connecting the radial functions of the hydrogen atom with the same principal number n but different orbital number l are deduced. In Sec. III we consider so(2,1) algebra of radial operators. We make the energy-dependent scaling to transform the set of hydrogen basis functions pertaining to the discrete part of the spectrum to the Sturmian basis set. It is shown that the existence of so(2,1) algebra implies recurrence relations connecting the radial functions with the same orbital number l but different principal number n. Finally, these relations are combined with the ones derived in Sec. II to deduce the relations that are advantageous for further calculations. The rest of the paper is devoted to the applications of these recurrence relations. In Sec. IV the calculation of the matrix elements of Coulomb interaction is described in detail. First, the multipole expansion of the Coulomb potential is used to separate the radial and angular degrees of freedom. Further, the product of two radial functions is written as a linear combination of the radial functions. Numerically stable recurrence relations for the coefficients of the linear combination are derived. The linearization of the product of radial functions is used to write the integrals over four radial functions as the linear combination of the integrals over two radial functions. From recurrence relations for the radial functions, the recurrence relations for the reduced integrals are derived. This section constitutes a major development of the computation of the radial integrals. In Sec. V the method developed in this paper is used for CI calculation of the $1\,^1S$, $2\,^3S$, and $2\,^3S$ states of helium. In Appendix A the algebra of the angular operators is studied and the action of the angular operators on the angular functions is determined. This appendix summarizes the results concerning the so(3) vector operators necessary for the purposes of this paper. Finally, in Appendix B the one-electron integrals needed in Sec. IV are calculated.

To make the paper understandable for wide audience we completely avoid all the nomenclature of the mathematical theory of Lie algebras. To understand this paper it is sufficient to know the basic notions of quantum mechanics such as commutator, eigenvectors, and eigenvalues. The atomic units and Einstein summation convention will be used throughout this paper.

II. HYDROGEN ATOM

In this section the algebraic solution of hydrogen atom is given. It is shown that the Runge-Lenz vector commutes with the Hamiltonian of the hydrogen atom and it is a special case of so(3) vector operator. The matrix elements of so(3) vector operators between spherical harmonics yield the energy spectrum and the recurrence relations for the radial functions of the hydrogen atom. These recurrence relations connect the radial functions with the same principal number n but different orbital numbers l. The matrix elements of so(3) vector operators between spherical harmonics needed in this section are derived in Appendix A.

A. Energy spectrum of the hydrogen atom

Let us consider the problem of the nonrelativistic hydrogen atom

$$H|n,l,m\rangle = -\frac{1}{2n^2}|n,l,m\rangle, \tag{1}$$

where the Hamiltonian is given by

$$H = -\frac{\nabla^2}{2} - \frac{1}{r}. \tag{2}$$

At this point we assume that n is a positive real number. Later on we show that n has to be a positive integer.

Because of the spherical symmetry of the problem, it is advantageous to make the transition between Cartesian and spherical coordinates

$$x_k = rn_k. \tag{3}$$

Here, r is the radial distance and n_k are components of the corresponding unit vector

$$\vec{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta). \tag{4}$$

Indices j, k and so on, range from 1 to 3. The letter i is reserved for the square-root of minus one.

Using the chain rule for the differentiation of composed functions, expression of the operator ∇_k in terms of the variables r, θ, and φ reads

$$\nabla_k = \frac{\partial}{\partial x_k} = n_k\frac{\partial}{\partial r} + \frac{\nabla_k^n}{r}. \tag{5}$$

Here, the angular differential operator ∇^n was introduced by

$$\nabla^n = \left(-\frac{\sin\varphi}{\sin\theta}\frac{\partial}{\partial\varphi} + \cos\varphi\cos\theta\frac{\partial}{\partial\theta}, \frac{\cos\varphi}{\sin\theta}\frac{\partial}{\partial\varphi} + \sin\varphi\cos\theta\frac{\partial}{\partial\theta}, -\sin\theta\frac{\partial}{\partial\theta}\right). \tag{6}$$

Decomposition of the operators $\vec{r}$ and ∇ into the radial and angular parts simplifies expressions for the operators representing other observables. This is described in detail in Appendix A.

We separate the radial and angular variables also in the wave function

$$\langle\vec{r}|n,l,m\rangle = \langle r|n,l\rangle\langle\vec{n}|l,m\rangle = R_{n,l}(r/n)Y_{l,m}(\vec{n}). \tag{7}$$

It will be clear later why we write the argument of the radial function as r/n. By inserting this separation into Eq. (1) and using Eqs. (A8) and (A9) of Appendix A, we obtain the well-known equation for the radial functions

$$\left[\frac{p_r^2}{2} + \frac{l(l+1)}{2r^2} - \frac{1}{r}\right]R_{n,l}(r/n) = -\frac{1}{2n^2}R_{n,l}(r/n). \tag{8}$$

Here, p_r denotes the radial momentum

$$p_r = -i\left(\frac{\partial}{\partial r} + \frac{1}{r}\right). \tag{9}$$

At this point, the differential equation (8) is usually solved. However, there is another approach based on the commutativity of the Runge-Lenz vector with the Hamiltonian (2). The latter approach will prove to be more advantageous when dealing with many-electron atoms.

The Runge-Lenz vector is given by

$$\vec{X} = \frac{1}{2}(\vec{L}\times\vec{p} - \vec{p}\times\vec{L}) + \vec{n}, \tag{10}$$

Using the decompositions (3) and (5), it can be rewritten into the more suitable form

$$\vec{X} = \vec{n}\left(-1 - \frac{\partial}{\partial r} + \frac{L^2}{r}\right) + \nabla^n\frac{\partial}{\partial r}. \tag{11}$$

Commutativity of the components of Runge-Lenz vector with Hamiltonian (2) can be proved using Eqs. (A14) and (A15) of Appendix A and Eq. (11).

It is seen from Eq. (11) that the Runge-Lenz vector acts on spherical harmonics in the same way as the operator

$$\vec{V} = f(r)\vec{n} + g(r)\nabla^n. \tag{12}$$

Here, $f(r)$ and $g(r)$ are operators acting on radial functions. It follows from the representation theory of so(4) algebra that the third component of the operator (12) acts on the spherical harmonics as [see Eqs. (A28) and (A32) of Appendix A]

$$V_3|l,m\rangle = c_l\sqrt{(l+m)(l-m)}|l-1,m\rangle + c_{l+1}\sqrt{(l+1+m)(l+1-m)}|l+1,m\rangle. \tag{13}$$

The coefficients c_l are determined from Eq. (A34) of Appendix A

$$c_l^2(2l-1)(l+m) + c_{l+1}^2(l+1-m)(2l+3) = \langle l,m|(V^2 - i[V_1,V_2])|l,m\rangle. \tag{14}$$

Runge-Lenz vector commutes with Hamiltonian (2). Thus, Eqs. (13) and (14) can be in this case written as

$$X_3|n,l,m\rangle = c_l^n\sqrt{(l+m)(l-m)}|n,l-1,m\rangle + c_{l+1}^n\sqrt{(l+1+m)(l+1-m)}|n,l+1,m\rangle \tag{15}$$

and

$$\begin{aligned}(c_l^n)^2(2l-1)(l+m) + (c_{l+1}^n)^2(l+1-m)(2l+3) &= \langle n,l,m|(X^2 - i[X_1,X_2])|n,l,m\rangle\\ &= \langle n,l,m|1 + 2H(L^2+1) - 2HL_3|n,l,m\rangle\\ &= \frac{n^2 - l(l+1) - 1 + m}{n^2}.\end{aligned} \tag{16}$$

Comparing the terms proportional to the zeroth and first power of m on both sides of the last equation yields

$$c_l^n = \frac{1}{n}\sqrt{\frac{(n-l)(n+l)}{(2l+1)(2l-1)}}. \tag{17}$$

Expressions for X^2 and $[X_1,X_2]$ used in Eq. (16) can be obtained from Eqs. (1) and (11) and from Eqs. (A1), (A2), (A4)–(A6), (A9), (A10), and (A13)–(A15) of Appendix A.

Since operator $\vec{X}$ is Hermitian and its third component is real, coefficients c_l^n have to be real. It is seen from the last equation and Eq. (15) that this holds only if the maximum allowed value of l for fixed n is $l=n-1$ and n is an integer. This finishes the derivation of Bohr formula for the energy levels of the hydrogen atom. The derivation given here is more or less the same as that of Pauli [14]. Let us also note that six operators $\vec{L}$ and $\vec{X}$ are closed under commutation. This is usually referred to as so(4) algebra [13].

B. Wave functions of the hydrogen atom

We would like to point out that we can also derive the form of radial functions $R_{n,l}(r)$ without solving Eq. (8). We compare the action of operator X_3 on the states $|n,l,m\rangle$ as calculated from Eq. (11) and from Eq. (15). To get the action of operator X_3 given by Eq. (11) we need to know the action of operators n_3 and ∇_3^n on spherical harmonics. Operator $\vec{n}$ is special case of operator (12). The matrix elements of the operator n_3 are given by Eqs. (13) and (14). Since obviously $n^2=1$ and $[n_1,n_2]=0$ we have

$$n_3|l,m\rangle = b_{l,m}|l-1,m\rangle + b_{l+1,m}|l+1,m\rangle, \tag{18}$$

where

$$b_{l,m} = \sqrt{\frac{(l+m)(l-m)}{(2l-1)(2l+1)}}. \tag{19}$$

The action of the third component of operator ∇^n follows from Eq. (A16) of Appendix A and Eq. (18)

$$\nabla_3^n|l,m\rangle = (l+1)b_{l,m}|l-1,m\rangle - l b_{l+1,m}|l+1,m\rangle. \qquad (20)$$

Using Eqs. (11), (18), and (20), we get that the third component of the Runge-Lenz vector acts on the states (7) as

$$\begin{aligned} X_3\langle\vec{r}|n,l,m\rangle &= \left(l\frac{d}{dr} - 1 + \frac{l(l+1)}{r}\right)R_{n,l}(r/n)b_{l,m}Y_{l-1,m}(\vec{n}) \\ &\quad - \left(-(l+1)\frac{d}{dr} - 1 + \frac{l(l+1)}{r}\right) \\ &\quad \times R_{n,l}(r/n)b_{l+1,m}Y_{l+1,m}(\vec{n}). \end{aligned} \qquad (21)$$

Finally, we insert the separation (7) into Eq. (15). Since the spherical harmonics form an orthonormal basis set, the terms proportional to $Y_{l-1,m}(\vec{n})$ in Eqs. (15) and (21) have to be equal:

$$\left(l\frac{d}{dr} - 1 + \frac{l(l+1)}{r}\right)R_{n,l}(r/n) = \frac{\sqrt{n^2-l^2}}{n}R_{n,l-1}(r/n). \qquad (22)$$

The terms proportional to $Y_{l+1,m}(\vec{n})$ in Eqs. (15) and (21) have to be equal as well, i.e.,

$$\begin{aligned} &\left((l+1)\frac{d}{dr} + 1 - \frac{l(l+1)}{r}\right)R_{n,l}(r/n) \\ &= -\frac{\sqrt{n^2-(l+1)^2}}{n}R_{n,l+1}(r/n). \end{aligned} \qquad (23)$$

Considering the last equation for $l=n-1$, we get the first order differential equation for the radial function $R_{n,n-1}(r)$, whose solution reads

$$R_{n,n-1}(r/n) = K_n(r/n)^{n-1}e^{-r/n}. \qquad (24)$$

Considering Eq. (22) for l descending from $n-1$ to 0, the remaining radial functions $R_{n,l}(r/n)$ are obtained by differentiation. Equations (22) and (23) were also derived in Ref. [18] from different considerations. In that paper it is described how these equations can be used for the calculation of the intensities of the hydrogen atom.

III. STURMIAN BASIS SET

In this section, the transition from the discrete part of the hydrogenic basis set to the Sturmian basis set is performed via energy-dependent scaling. The ladder operators for the radial functions are constructed. These operators yield the recurrence relations for the radial functions with the same orbital number l. These recurrence relations for the radial functions are combined with those derived in the previous Section to generate additional recurrence relations. Finally, the orthonormality relations of the Sturmian basis set are discussed.

A. Energy-dependent scaling

For variational calculation of the more complicated atoms the hydrogenic functions are not convenient. The reason is that the Hamiltonian given by Eq. (2) has both discrete and continuous spectra. Therefore, the discrete spectrum does not form a complete basis set. The incompleteness of the discrete hydrogenic functions is caused by the presence of factor $1/n$ in the argument of the exponential function, see Eq. (24). Therefore we make the energy-dependent scaling $r \to rn$. Equation (8) then takes the form

$$\left[\frac{p_r^2}{2} + \frac{l(l+1)}{2r^2} - \frac{n}{r}\right]R_{n,l}(r) = -\frac{1}{2}R_{n,l}(r). \qquad (25)$$

In Eq. (8), we considered different energy levels labeled by n for fixed nuclear charge $Z=1$, while in Eq. (25), we consider different nuclear charges $Z=n$ for fixed energy level $E=-1/2$.

If we multiply Eq. (25) by r we can rewrite it into the form of the eigenvalue problem

$$T_3R_{n,l}(r) = nR_{n,l}(r), \qquad (26)$$

where

$$T_3 = \frac{r}{2}\left(p_r^2 + \frac{l(l+1)}{r^2}\right) + \frac{r}{2}. \qquad (27)$$

B. Ladder operators for radial functions

The great advantage of Eq. (26) is that the spectrum of operator T_3 is purely discrete. This is most easily seen by constructing step-up and step-down operators

$$T_\pm = \frac{r}{2}\left(p_r^2 + \frac{l(l+1)}{r^2}\right) - \frac{r}{2} \pm irp_r. \qquad (28)$$

It follows from Eqs. (27) and (28) that

$$[T_3, T_\pm] = \pm T_\pm. \qquad (29)$$

Acting with this operator equation on the radial functions $R_{n,l}(r)$, we get (see, e.g., Refs. [13,19,20])

$$T_\pm R_{n,l}(r) = \sqrt{(n \pm l \pm 1)(n \mp l)}R_{n\pm1,l}(r). \qquad (30)$$

Operators T_3 and $T_\pm$ are closed under commutation. This is related to the existence of the radial so(2,1) algebra, as detailed in Refs. [13,17,19]. With the help of operators T_3 and $T_\pm$ we can, for example, determine action of the radial coordinate and derivative with respect to radial coordinate on the radial functions, namely,

$$\begin{aligned} 2rR_{n,l}(r) &= (2T_3 - T_+ - T_-)R_{n,l}(r) \\ &= 2nR_{n,l}(r) - \sqrt{(n+l+1)(n-l)}R_{n+1,l}(r) \\ &\quad - \sqrt{(n-l-1)(n+l)}R_{n-1,l}(r) \end{aligned} \qquad (31)$$

and

$$\begin{aligned} 2r\left(\frac{d}{dr} + \frac{1}{r}\right)R_{n,l}(r) &= (T_+ - T_-)R_{n,l}(r) \\ &= \sqrt{(n+l+1)(n-l)}R_{n+1,l}(r) \\ &\quad - \sqrt{(n-l-1)(n+l)}R_{n-1,l}(r), \end{aligned} \qquad (32)$$

respectively. These equations follow from Eqs. (9), (26)–(28), and (30).

C. Recurrence relations

In the previous section we derived recurrence relations for the radial functions of hydrogen, Eqs. (22) and (23). By making energy-dependent scaling $r \rightarrow rn$ in these equations we convert them to the equations for the Sturmian radial functions

$$\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)-\frac{n}{l}r+l\right]R_{n,l}(r)=\frac{\sqrt{n^2-l^2}}{l}rR_{n,l-1}(r) \quad (33)$$

and

$$\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)+\frac{n}{l+1}r-(l+1)\right]R_{n,l}(r) = \frac{\sqrt{n^2-(l+1)^2}}{l+1}rR_{n,l+1}(r). \quad (34)$$

Thus, Eqs. (31) and (32) connect the radial functions with the same l and different n. The last two equations connect the radial functions with the same n and different l. We could have finished at this point. However, for the purposes of the following Section it is advantageous to combine Eqs. (31)–(34) to additional recurrence relations.

We apply Eqs. (31) and (32) to the left-hand side of the last two equations. After some manipulation we obtain

$$\begin{aligned}2rR_{n,l}(r) &= \sqrt{(n+l+1)(n+l+2)}R_{n+1,l+1}(r)\\ &\quad+\sqrt{(n-l-2)(n-l-1)}R_{n-1,l+1}(r)\\ &\quad-2\sqrt{n^2-(l+1)^2}R_{n,l+1}(r)\end{aligned} \quad (35)$$

and

$$\begin{aligned}2rR_{n,l}(r) &= \sqrt{(n-l)(n+1-l)}R_{n+1,l-1}(r)\\ &\quad+\sqrt{(n+l)(n+l-1)}R_{n-1,l-1}(r)-2\sqrt{n^2-l^2}R_{n,l-1}(r).\end{aligned} \quad (36)$$

Further, we rewrite Eqs. (33) and (34):

$$r\left(\frac{d}{dr}+\frac{l+1}{r}\right)R_{n,l}(r)=\frac{\sqrt{n^2-l^2}}{l}rR_{n,l-1}(r)+\frac{n}{l}rR_{n,l}(r) \quad (37)$$

and

$$r\left(\frac{d}{dr}-\frac{l}{r}\right)R_{n,l}(r)=\frac{\sqrt{n^2-(l+1)^2}}{l+1}rR_{n,l+1}(r)+\frac{n}{l+1}rR_{n,l}(r) \quad (38)$$

and arrange the right-hand sides of the last two equations as follows. In Eq. (37) we use Eq. (31) on the first term and Eq. (36) on the second term. In Eq. (38) we use Eq. (31) on the first term and Eq. (35) on the second term. After some manipulation we get

$$\begin{aligned}2r\left(\frac{d}{dr}-\frac{l}{r}\right)R_{n,l}(r) &= -\sqrt{(n+l+1)(n+l+2)}R_{n+1,l+1}(r)\\ &\quad+\sqrt{(n-l-2)(n-l-1)}R_{n-1,l+1}(r)\end{aligned} \quad (39)$$

and

$$\begin{aligned}2r\left(\frac{d}{dr}+\frac{l+1}{r}\right)R_{n,l}(r) &= -\sqrt{(n-l)(n+1-l)}R_{n+1,l-1}(r)\\ &\quad+\sqrt{(n+l)(n+l-1)}R_{n-1,l-1}(r).\end{aligned} \quad (40)$$

Equations (31), (32), (35), (36), (39), and (40) will be used for the calculation of one- and two-electron integrals in the next section.

D. Orthonormality relations

Since functions $R_{n,l}(r)$ are eigenfunctions of Hermitian operator T_3, they form an orthonormal basis set. However, in contrast to the Hamilton operator (2) that is Hermitian with respect to the inner product

$$\langle n_1,l|H|n_2,l\rangle=\int_0^\infty r^2R_{n_1,l}(r)HR_{n_2,l}(r)dr, \quad (41)$$

operator T_3 is Hermitian with respect to the inner product

$$(n_1,l|T_3|n_2,l)=\int_0^\infty rR_{n_1,l}(r)T_3R_{n_2,l}(r)dr. \quad (42)$$

Consequently, while the wave functions of hydrogen are orthonormal with respect to the inner product

$$\langle n_1,l|n_2,l\rangle=\int_0^\infty r^2R_{n_1,l}(r)R_{n_2,l}(r)dr=\delta_{n_1,n_2}, \quad (43)$$

the eigenfunctions $R_{n,l}(r)$ of operator T_3 are orthonormal with respect to the inner product

$$(n_1,l|n_2,l)=\int_0^\infty rR_{n_1,l}(r)R_{n_2,l}(r)dr=\delta_{n_1,n_2}. \quad (44)$$

IV. MATRIX ELEMENTS OF THE COULOMB INTERACTION

In this section, we apply results of the previous section to the calculation of two-electron integrals. First, as usually, we separate the radial and angular degrees of freedom by means of the multipole expansion. Further, we write the product of two radial functions as a linear combination of radial functions. We thus reduce the integrals over four radial functions to the integrals over two radial functions. For these reduced integrals, we derive recurrence relations combining integration by parts with algebraic methods. Using result of this section calculation of two-electron integrals is reduced to the calculation of one-electron integrals. Evaluation of one-electron integrals is described in Appendix B.

A. Screened radial functions

In many-electrons atoms the electrons occupying different orbitals "see" different effective nuclear charges. For example, the dominant configuration of P states of two electron atoms is the one in which the first electron occupies the s orbital and the second electron occupies the p orbital. Now, the electron occupying the s orbital is close to the nucleus and its effective nuclear charge is close to the nuclear charge Z. However, the electron occupying the p orbital is further away from the nucleus and "sees" the charge Z of nucleus "screened" by the charge of the electron in s orbital -1. Its effective nuclear charge is therefore close to $Z-1$. Thus, to get fast convergence of the variational method, we have to consider different screening constants for different electrons.

For this purpose, instead of the "ordinary" radial functions $R_{n,l}(r)$, we consider the "screened" radial functions $R_{n,l}(\xi r)$. The "screened" functions are obtained from "ordinary" functions by the energy-independent scaling $r \rightarrow \xi r$ and multiplication by ξ. This multiplication is to ensure the proper normalization (44). For example, the nodeless "screened" functions $R_{l+1,l}(\xi r)$ read

$$R_{l+1,l}(\xi r) = \frac{2\xi}{\sqrt{(2l+1)!}}(2\xi r)^l e^{-\xi r}. \qquad (45)$$

This equation is obtained from Eq. (24) for $r \rightarrow rn\xi$ and from Eq. (44).

B. Separation of radial and angular degrees of freedom

Calculating the matrix elements of the Coulomb interaction between two spin orbitals leads to the calculation of the integrals

$$\int d^3r_1 \int d^3r_2 R_{n_{1k},l_{1k}}(r_1\xi_{1k}) Y_{l_{1k},m_{1k}}(\vec{n}_1) R_{n_{2k},l_{2k}}(r_2\xi_{2k}) \times Y_{l_{2k},m_{2k}}(\vec{n}_2) r_{12}^{-1} R_{n_{1j},l_{1j}}(r_1\xi_{1j}) Y_{l_{1j},m_{1j}}(\vec{n}_1) R_{n_{2j},l_{2j}}(r_2\xi_{2j}) \times Y_{l_{2j},m_{2j}}(\vec{n}_2). \qquad (46)$$

To separate the angular and radial degrees of freedom, we expand r_{12}^{-1} in the multipole expansion

$$r_{12}^{-1} = \frac{1}{r_>}\sum_{l=0}^{\infty}\left(\frac{r_<}{r_>}\right)^l P_l(\vec{n}_1 \cdot \vec{n}_2), \qquad (47)$$

where $r_< = r_1$, $r_> = r_2$ if $r_1 < r_2$ and $r_< = r_2$, $r_> = r_1$ if $r_1 > r_2$. Here, $P_l(x)$ denotes the Legendre polynomials.

The angular part of the integration is achieved by the methods developed by Racah, see, e.g., Refs. [9–11]. The radial part of the integration involves calculation of integrals

$$\int_0^\infty dr_1 R_{n_{1k},l_{1k}}(r_1\xi_{1k}) R_{n_{1j},l_{1j}}(r_1\xi_{1j}) r_1^{l+2} \times \int_{r_1}^\infty dr_2 R_{n_{2k},l_{2k}}(r_2\xi_{2k}) R_{n_{2j},l_{2j}}(r_2\xi_{2j}) r_2^{-l+1} + \int_0^\infty dr_1 R_{n_{1k},l_{1k}}(r_1\xi_{1k}) R_{n_{1j},l_{1j}}(r_1\xi_{1j}) r_1^{-l+1} \times \int_0^{r_1} dr_2 R_{n_{2k},l_{2k}}(r_2\xi_{2k}) R_{n_{2j},l_{2j}}(r_2\xi_{2j}) r_2^{l+2}. \qquad (48)$$

C. Linearization of the product of two functions

It has been pointed out in Ref. [17], that the products of the radial functions of the same variable [such as $R_{n_{1k},l_{1k}}(r_1\xi_{1k}) R_{n_{1j},l_{1j}}(r_1\xi_{1j})$] appear in the integrals (48). The integration of the product of three spherical harmonics is greatly simplified by virtue of the fact that the product of two spherical harmonics can be written as a linear combination of spherical harmonics. This is known as a special case of the Wigner-Eckart theorem. Being inspired by that theorem, we write

$$r^p R_{n_1,l_1}(\xi_1 r) R_{n_2,l_2}(\xi_2 r) = \sum_{n=l'+1}^{n_1+n_2-1+p} (n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p R_{n,l'}(\xi r), \qquad (49)$$

where $l' = l_1 + l_2$ and $\xi = \xi_1 + \xi_2$. The number of the nodes of function $R_{n,l'}(\xi r)$ is $n - l' - 1$. The product of the function with $n_1 - l_1 - 1$ nodes and the function with $n_2 - l_2 - 1$ nodes is the function with $n_1 + n_2 - 1 - l' - 1$ nodes. Thus, this function is composed only of the functions $R_{n,l'}(\xi r)$ for which the number of nodes $n - l' - 1$ does not exceed $n_1 + n_2 - 1 - l' - 1$. Thus, the upper bound in the summation in Eq. (49) is $n = n_1 + n_2 - 1$ for $p=0$. For a nonzero p the upper bound is deduced from Eq. (31).

Let us determine coefficients $(n_1, l_1, \xi_1, n_2, l_2, \xi_2|n)_p$. Multiplying Eq. (49) by $rR_{n',l'}(\xi r)$, integrating over r and using the orthonormality of radial functions, (44), we obtain

$$(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n')_p = \int_0^\infty r^{p+1} R_{n',l'}(\xi r) R_{n_1,l_1}(\xi_1 r) R_{n_2,l_2}(\xi_2 r)\, dr. \qquad (50)$$

Further, we multiply Eq. (49) by $2r$. On the left-hand side of Eq. (49) we let $2r$ act on the function $R_{n_1,l_1}(\xi_1 r)$ according to Eq. (31) where we substitute $r \rightarrow \xi_1 r$. On the right-hand side of Eq. (49) operator $2r$ acts on function $R_{n,l'}(\xi r)$. Thus we arrive at equation

$$r^p R_{n_2,l_2}(\xi_2 r)\frac{1}{\xi_1}[2n_1 R_{n_1,l_1}(\xi_1 r) - \sqrt{(n_1+l_1+1)(n_1-l_1)}R_{n_1+1,l_1}(\xi_1 r) - \sqrt{(n_1-l_1-1)(n_1+l_1)}R_{n_1-1,l_1}(\xi_1 r)]$$

$$= \sum_{n=l'+1}^{n_1+n_2-1+p} (n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p \frac{1}{\xi} \times [2nR_{n,l'}(\xi r) - \sqrt{(n+l'+1)(n-l')}R_{n+1,l'}(\xi r) - \sqrt{(n-l'-1)(n+l')}R_{n-1,l'}(\xi r)]. \quad (51)$$

We multiply the last equation by $rR_{n',l'}(\xi r)$, integrate over r and use the orthonormality relations (44) and Eq. (50):

$$2n_1(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n') - \sqrt{(n_1+l_1+1)(n_1-l_1)}(n_1+1,l_1,\xi_1,n_2,l_2,\xi_2|n') - \sqrt{(n_1-l_1-1)(n_1+l_1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n') = \sum_{n=l'+1}^{n_1+n_2-1+p} (n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p \frac{\xi_1}{\xi} \times [2n\delta_{n',n} - \sqrt{(n+l'+1)(n-l')}\delta_{n',n+1} - \sqrt{(n-l'-1)(n+l')}\delta_{n',n-1}]. \quad (52)$$

After deleting the zero terms on the right-hand side, we obtain the following recurrence relation for the coefficients $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)$

$$(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p\sqrt{(n_1-l_1-1)(n_1+l_1)} = 2\left(n_1-1-\frac{\xi_1 n}{\xi}\right)(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p - \sqrt{(n_1+l_1-1)(n_1-l_1-2)}(n_1-2,l_1,\xi_1,n_2,l_2,\xi_2|n)_p + \frac{\xi_1}{\xi}\sqrt{(n+l')(n-l'-1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n-1)_p + \frac{\xi_1}{\xi}\sqrt{(n-l')(n+l'+1)}(n_1-1,l_1,\xi_1,n_2,l_2,\xi_2|n+1)_p. \quad (53)$$

The last equation expresses coefficients $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p$ through coefficients $(n_1',l_1,\xi_1,n_2,l_2,\xi_2|n')_p$ with n_1' smaller than n_1, but with n' sometimes smaller and sometimes larger than n. But since there are lower and upper bounds on the possible values of n, see Eq. (49), Eq. (53) can be used to lower the quantum number n_1 to l_1+1. To lower the quantum number n_2 to l_2+1 we apply Eq. (53) again exchanging this time n_1 and n_2, l_1 and l_2, and ξ_1 and ξ_2 and taking into account that $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p=(n_2,l_2,\xi_2,n_1,l_1,\xi_1|n)_p$.

The value of coefficients $(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|n)_p$ is obtained by inserting Eq. (45) into Eq. (49). We thus obtain

$$(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|l_1+l_2+1)_0 = \frac{2\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+1}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}} \quad (54)$$

and

$$(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|n)_0 = 0, n > l_1+l_2+1. \quad (55)$$

The case of a nonzero p is obtained from Eqs. (49) and (31). For example,

$$(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|l_1+l_2+1)_1 = 2(l_1+l_2+1)\frac{\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+2}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}}, \quad (56)$$

$$(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|l_1+l_2+2)_1 = -\sqrt{2(l_1+l_2+1)}\frac{\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+2}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}}, \quad (57)$$

and

$$(l_1+1,l_1,\xi_1,l_2+1,l_2,\xi_2|n)_1 = 0, \quad n > l_1+l_2+2. \quad (58)$$

Remarkably, the described method of calculating coefficients $(n_1,l_1,\xi_1,n_2,l_2,\xi_2|n)_p$ is numerically stable.

Using Eq. (49) for $p=1$, the integrals (48) can be written as linear combination of the integrals [17]

$$P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2) + P^{L_2,L_1,l}_{N_2,N_1}(\xi_2,\xi_1). \quad (59)$$

Here,

$$P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2) = \int_0^\infty \tilde{R}_{N_1,L_1}(\xi_1 r_1) r_1^{l+1}\int_{r_1}^\infty \tilde{R}_{N_2,L_2}(\xi_2 r_2) r_2^{-l}\, dr_2\, dr_1 \quad (60)$$

and

$$P^{L_2,L_1,l}_{N_2,N_1}(\xi_2,\xi_1) = \int_0^\infty \tilde{R}_{N_1,L_1}(\xi_1 r_1) r_1^{-l} \times \int_0^{r_1} \tilde{R}_{N_2,L_2}(\xi_2 r_2) r_2^{l+1}\, dr_2\, dr_1, \quad (61)$$

where we introduced the unnormalized radial functions $\tilde{R}_{n,l}(r)$ related to the normalized functions $R_{n,l}(r)$ via relation

$$\tilde{R}_{n,l}(r) = \sqrt{\frac{(n+l)!}{(n-l-1)!}}R_{n,l}(r). \quad (62)$$

By using unnormalized functions the irrational factors are conveniently eliminated.

The great advantage of our procedure is that the integrals (60) can be evaluated much more easily than the original integrals (48). In the next subsection, we derive recurrence relations for these integrals.

D. Recurrence relations for the integrals

1. Recurrence relations connecting integrals with different values of N_2 and L_2

The recurrence relations connecting integrals (60) with different values of N_2 and L_2 are derived from "analytic" equation [17]

$$\int_{r_1}^{\infty} r_2\left(\frac{d}{dr_2}+\frac{1}{r_2}\right)[r_2^{-l}\widetilde{R}_{N_2,L_2}(\xi_2 r_2)]dr_2=-r_1^{-l+1}\widetilde{R}_{N_2,L_2}(\xi_2 r_1) \tag{63}$$

obtained by integration by parts and from the "algebraic" equations

$$2r\left(\frac{d}{dr}+\frac{1}{r}\right)\widetilde{R}_{n,l}(\xi r)=(n-l)\widetilde{R}_{n+1,l}(\xi r)-(n+l)\widetilde{R}_{n-1,l}(\xi r), \tag{64}$$

$$2r\left(\frac{d}{dr}-\frac{l}{r}\right)\widetilde{R}_{n,l}(r)=-\widetilde{R}_{n+1,l+1}(r)+\widetilde{R}_{n-1,l+1}(r), \tag{65}$$

and

$$2r\left(\frac{d}{dr}+\frac{l+1}{r}\right)\widetilde{R}_{n,l}(r)=-(n-l)(n+1-l)\widetilde{R}_{n+1,l-1}(r)+(n+l)\times(n+l-1)\widetilde{R}_{n-1,l-1}(r). \tag{66}$$

Equations (64)–(66) are obtained by substituting Eq. (62) into Eqs. (32), (39), and (40).

Inserting Eqs. (64)–(66) into Eq. (63), multiplying Eq. (63) by $2\widetilde{R}_{N_1,L_1}(r_1\xi_1)r_1^{l+1}$ and integrating over r_1 from zero to infinity we obtain successively

$$\begin{aligned}&-(N_2+L_2)P_{N_1,N_2-1}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad+(N_2-L_2)P_{N_1,N_2+1}^{L_1,L_2,l}(\xi_1,\xi_2)-2lP_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad=-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{67}$$

$$\begin{aligned}&P_{N_1,N_2-1}^{L_1,L_2+1,l}(\xi_1,\xi_2)\\&\quad-P_{N_1,N_2+1}^{L_1,L_2+1,l}(\xi_1,\xi_2)+2(L_2+1-l)P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad=-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{68}$$

and finally

$$\begin{aligned}&(N_2+L_2)(N_2+L_2-1)P_{N_1,N_2-1}^{L_1,L_2-1,l}(\xi_1,\xi_2)\\&\quad-(N_2-L_2)(N_2-L_2+1)P_{N_1,N_2+1}^{L_1,L_2-1,l}(\xi_1,\xi_2)-2(L_2\\&\quad+l)P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad=-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned} \tag{69}$$

The one-electron integrals on the right-hand side of these equations are given as

$$(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2)=\int_0^{\infty}2r^2\widetilde{R}_{N_1,L_1}(\xi_1 r)\widetilde{R}_{N_2,L_2}(\xi_2 r)dr. \tag{70}$$

2. Recurrence relations connecting integrals with different values of N_1 and L_1

To derive recurrence relations connecting the integrals (60) with different values of N_1 and L_1, we need a modification of "analytic" equation (63), namely [17]

$$\begin{aligned}&\int_0^{\infty}dr_1\, r_1\left(\frac{d}{dr_1}+\frac{1}{r_1}\right)[r_1^{l+1}\widetilde{R}_{N_1,L_1}(\xi_1 r_1)]\int_{r_1}^{\infty}dr_2\,\widetilde{R}_{N_2,L_2}(\xi_2 r_2)r_2^{-l}\\&\quad=\int_0^{\infty}dr_1 r_1^2\widetilde{R}_{N_1,L_1}(\xi_1 r_1)\widetilde{R}_{N_2,L_2}(\xi_2 r_1)\end{aligned} \tag{71}$$

obtained by integration by parts. By inserting the "algebraic" equations (64)–(66) into Eq. (71) we obtain

$$\begin{aligned}&-(N_1+L_1)P_{N_1-1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad+(N_1-L_1)P_{N_1+1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)+2(l+1)P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad=(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{72}$$

$$\begin{aligned}&P_{N_1-1,N_2}^{L_1+1,L_2,l}(\xi_1,\xi_2)\\&\quad-P_{N_1+1,N_2}^{L_1+1,L_2,l}(\xi_1,\xi_2)+2(L_1+l+2)P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad=(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2),\end{aligned} \tag{73}$$

and, finally,

$$\begin{aligned}&(N_1+L_1)(N_1+L_1-1)P_{N_1-1,N_2}^{L_1-1,L_2,l}(\xi_1,\xi_2)\\&\quad-(N_1-L_1)(N_1-L_1+1)P_{N_1+1,N_2}^{L_1-1,L_2,l}(\xi_1,\xi_2)\\&\quad+2(l+1-L_1)P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)\\&\quad=(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned} \tag{74}$$

3. Discussion

By means of recurrence relations for the radial functions, we have derived recurrence relations for the integrals. We note that Eq. (67) and (72) were derived already in Ref. [17]. As is clear from the above derivation, these equations result from Eq. (64). The latter can be traced back to commutation relations (29). Equation (64) connects the radial functions with different principle numbers n but the same orbital number l. Consequently, Eqs. (67) and (72) connect the values of integrals $P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)$ with different principal numbers N_1 and N_2, but with the same orbital numbers L_1 and L_2. On the other hand, Eqs. (68), (69), (73), and (74) are derived for the first time here. They result from Eqs. (65) and (66). The latter can be traced back to the commutation relations between operators pertaining to so(4) algebra. Equations (65) and (66) connect the radial functions with different principle numbers n and with different orbital number l. Consequently, Eqs. (68), (69), (73), and (74) connect the values of integrals $P_{N_1,N_2}^{L_1,L_2,l}(\xi_1,\xi_2)$ with different principal numbers N_1 and N_2 and with different orbital numbers L_1 and L_2.

In Ref. [17] we found by experimentation with MAPLE that Eqs. (67) and (72) acquire very simple solution in the cases when the right-hand side vanishes. This appears either for $\xi_1=\xi_2$, $L_1=L_2$ and $|N_1-N_2|>1$, see Eqs. (44) and (31), or for $\xi_1=\xi_2$, $L_1<L_2$ and $N_1>N_2+1$, see discussion after Eq. (B12) below. Further, we found that integrals $P_{N_1,N_2}^{l,L_2,l}(\xi_1,\xi_1)$ vanish for $N_1>N_2$. At that time we did not know Eqs. (68), (69), (73), and (74). The information found by experimentation is contained in these equations.

Now, we have to use Eqs. (67)–(74) for the actual calculation of integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ in such a way that the simplification mentioned above comes out in a numerical stable way. For example, as mentioned above, integrals $P^{l,L_2,l}_{N_1,N_2}(\xi_1,\xi_1)$ equal zero for $N_1>N_2$. This zero cannot result from a subtraction of two large numbers.

With this in mind we combine Eqs. (67) and (68) into a single equation

$$\begin{aligned}&-2lP^{L_1,L_2+1,l}_{N_1,N_2}(\xi_1,\xi_2)-2(L_2+1)P^{L_1,L_2+1,l}_{N_1,N_2+1}(\xi_1,\xi_2)\\&\quad+2(L_2+1-l)(N_2+L_2+1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=-(N_1,L_1,\xi_1|2r|N_2,L_2+1,\xi_2)\\&\qquad-(N_2+L_2+1)(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned}\tag{75}$$

The right-hand side of this equation can be brought into the form

$$\begin{aligned}&-\frac{2(L_2+1)}{\xi_2}[(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)\\&\qquad-(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)],\end{aligned}$$

where

$$(N_1,L_1,\xi_1|N_2,L_2,\xi_2)=\int_0^\infty r\widetilde{R}_{N_1,L_1}(\xi_1 r)\widetilde{R}_{N_2,L_2}(\xi_2 r)dr.\tag{76}$$

Here, we used equations

$$\begin{aligned}2\xi_2 r\widetilde{R}_{N_2,L_2}(\xi_2 r)&=\widetilde{R}_{N_2+1,L_2+1}(\xi_2 r)+\widetilde{R}_{N_2-1,L_2+1}(\xi_2 r)\\&\quad-2\widetilde{R}_{N_2,L_2+1}(\xi_2 r)\end{aligned}\tag{77}$$

and

$$\begin{aligned}&2\xi_2 r\widetilde{R}_{N_2,L_2+1}(\xi_2 r)\\&\quad=2N_2\widetilde{R}_{N_2,L_2+1}(\xi_2 r)\\&\qquad-(N_2-L_2-1)\widetilde{R}_{N_2+1,L_2+1}(\xi_2 r)\\&\qquad-(N_2+L_2+1)\widetilde{R}_{N_2-1,L_2+1}(\xi_2 r).\end{aligned}\tag{78}$$

These equations were obtained by substituting Eq. (62) into Eqs. (31) and (35), respectively.

Further, we combine Eqs. (67) and (69) into a single equation

$$\begin{aligned}&2L_2(N_2+L_2-1)P^{L_1,L_2-1,l}_{N_1,N_2-1}(\xi_1,\xi_2)\\&\quad-2l(N_2-L_2)P^{L_1,L_2-1,l}_{N_1,N_2}(\xi_1,\xi_2)-2(L_2+l)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=-(N_1,L_1,\xi_1|2r|N_2,L_2-1,\xi_2)(N_2-L_2)\\&\qquad-(N_1,L_1,\xi_1|2r|N_2,L_2,\xi_2).\end{aligned}\tag{79}$$

The right-hand side of this equation can be simplified into the form

$$\begin{aligned}&-\frac{2L_2}{\xi_2}[(N_2+L_2-1)(N_1,L_1,\xi_1|N_2-1,L_2-1,\xi_2)\\&\qquad-(N_2-L_2)(N_1,L_1,\xi_1|N_2,L_2-1,\xi_2)].\end{aligned}$$

Here we used Eq. (78) and equation

$$\begin{aligned}2\xi_2 r\widetilde{R}_{N_2,L_2}(\xi_2 r)&=(N_2-L_2+1)(N_2-L_2)\widetilde{R}_{N_2+1,L_2-1}(\xi_2 r)\\&\quad+(N_2+L_2)(N_2+L_2-1)\widetilde{R}_{N_2-1,L_2-1}(\xi_2 r)\\&\quad-2(N_2+L_2)(N_2-L_2)\widetilde{R}_{N_2,L_2-1}(\xi_2 r).\end{aligned}\tag{80}$$

This equation is obtained by inserting Eq. (62) into Eq. (36).

Similarly, we put together Eqs. (72) and (73)

$$\begin{aligned}&-2(L_1+1)P^{L_1+1,L_2,l}_{N_1+1,N_2}(\xi_1,\xi_2)+2(l+1)P^{L_1+1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad+2(L_1+l+2)(N_1+L_1+1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=\frac{2(L_1+1)}{\xi_1}[(N_1+1,L_1+1,\xi_1|N_2,L_2,\xi_2)\\&\qquad-(N_1,L_1+1,\xi_1|N_2,L_2,\xi_2)],\end{aligned}\tag{81}$$

and Eqs. (72) and (74)

$$\begin{aligned}&2L_1(N_1+L_1-1)P^{L_1-1,L_2,l}_{N_1-1,N_2}(\xi_1,\xi_2)+2(N_1-L_1)(l+1)\\&\quad\times P^{L_1-1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)+2(l+1-L_1)P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)\\&\quad=\frac{2L_1}{\xi_1}[(N_1+L_1-1)(N_1-1,L_1-1,\xi_1|N_2,L_2,\xi_2)\\&\qquad-(N_1-L_1)(N_1,L_1-1,\xi_1|N_2,L_2,\xi_2)].\end{aligned}\tag{82}$$

We note that considering the last equation for $\xi_2=\xi_1$ and $L_1=l+1$ together with orthonormality relations (44) yields $P^{l,L_2,l}_{N_1,N_2}(\xi_1,\xi_1)=0$ in a numerically stable way, as desired.

E. Actual calculations of the integrals

The above equations can be used for actual calculations of the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ as follows. We set $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)=0$ whenever $N_1<L_1+1$ or $N_2<L_2+1$. Further, we assume that we know how to calculate the one-electron integrals $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)$. Calculation of these integrals is left to Appendix B.

1. Case $L_1\neq L_2$

We can use Eq. (81) repeatedly to lower the value of L_1 to l and to consider Eq. (82) for $L_1=l+1$ to calculate the integrals $P^{l,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$. Similarly, we can use Eq. (75) repeatedly to lower the value of L_2 to l and to consider Eq. (75) for $L_2=l-1$ to calculate the integrals $P^{L_1,l,l}_{N_1,N_2}(\xi_1,\xi_2)$. However, this way of calculation of the integrals changes the difference L_1-L_2. This is not advantageous because of the following reason. As mentioned above, the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ have particularly simple form for $\xi_1=\xi_2$ and $L_1=L_2$. Proceeding in this way we would calculate simple integrals $P^{L_1,L_1,l}_{N_1,N_2}(\xi_1,\xi_1)$ through the more complicated integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_1)$ with $L_1\neq L_2$.

The better way is to reduce the integrals with $L_1 \neq L_2$ only to the case $L_1 = L_2$. In the case L_1 greater than L_2 we use Eq. (81) repeatedly to lower the value of L_1 to L_2. In the opposite case L_2 greater than L_1 we use Eq. (75) to lower the value of L_2 to L_1.

2. *Case $L_1 = L_2 > l$*

Further, we show that the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ for the case $L_1 = L_2 > l$ can be reduced to the integrals $P^{L_1,L_2,l}_{N_1,N_2}(\xi_1,\xi_2)$ with $L_1 = L_2 = l$. We set $L_1 = L$ and $L_2 + 1 = L$ in Eqs. (75) and (82). We eliminate the integrals $P^{L,L-1,l}_{N_1,N_2}(\xi_1,\xi_2)$ from these equations and obtain

$$\begin{aligned} & L P^{L,L,l}_{N_1,N_2+1}(\xi_1,\xi_2) + l P^{L,L,l}_{N_1,N_2}(\xi_1,\xi_2) \\ & \quad - \frac{L}{\xi_2}[(N_1,L,\xi_1|N_2+1,L,\xi_2) - (N_1,L,\xi_1|N_2,L,\xi_2)] \\ & = \frac{(L-l)(N_2+L)}{l+1-L}\Bigg\{ -L(N_1+L-1)P^{L-1,L-1,l}_{N_1-1,N_2}(\xi_1,\xi_2) \\ & \quad - (N_1-L)(l+1)P^{L-1,L-1,l}_{N_1,N_2}(\xi_1,\xi_2) \\ & \quad + \frac{L}{\xi_1}[(N_1+L-1)(N_1-1,L-1,\xi_1|N_2,L-1,\xi_2) \\ & \quad - (N_1-L)(N_1,L-1,\xi_1|N_2,L-1,\xi_2)]\Bigg\}. \end{aligned} \tag{83}$$

This equation cannot be used in the case $L = l+1$, since the denominator on the right-hand side vanishes.

Further, we set $L_1 + 1 = L$ and $L_2 = L$ in Eqs. (79) and (81). We eliminate integrals $P^{L-1,L,l}_{N_1,N_2}(\xi_1,\xi_2)$ from these equations and obtain

$$\begin{aligned} & L P^{L,L,l}_{N_1+1,N_2}(\xi_1,\xi_2) - (l+1) P^{L,L,l}_{N_1,N_2}(\xi_1,\xi_2) \\ & \quad + \frac{L}{\xi_1}[(N_1+1,L,\xi_1|N_2,L,\xi_2) - (N_1,L,\xi_1|N_2,L,\xi_2)] \\ & = \frac{(L+l+1)(N_1+L)}{l+L}\Bigg\{ -L(N_2+L-1)P^{L-1,L-1,l}_{N_1,N_2-1}(\xi_1,\xi_2) \\ & \quad + l(N_2-L)P^{L-1,L-1,l}_{N_1,N_2}(\xi_1,\xi_2) \\ & \quad + \frac{L}{\xi_2}[(N_2+L-1)(N_1,L-1,\xi_1|N_2,L-1,\xi_2) \\ & \quad - (N_2-L)(N_1,L-1,\xi_1|N_2,L-1,\xi_2)]\Bigg\}. \end{aligned} \tag{84}$$

This equation can be used in all cases.

Using Eqs. (83) and (84) we calculate integrals $P^{L,L,l}_{N_1,N_2}(\xi_1,\xi_2)$ through integrals $P^{L-k,L-k,l}_{N_1,N_2}(\xi_1,\xi_2)$. In actual calculation we use Eq. (83) in cases $N_2 < N_1$ and $L \neq l+1$. Otherwise we use Eq. (84). These equations are used repeatedly until $L-k = l$.

The advantage of Eqs. (83) and (84) is that they calculate integrals $P^{L_1,L_2}_{N_1,N_2}(\xi_1,\xi_2)$ where $L_1 = L_2$ through the integrals with different quantum numbers N_1, N_2, L_1, and L_2, but again with $L_1 = L_2$. The advantage of this approach becomes apparent when considering the case $\xi_1 = \xi_2$. By virtue of the orthonormality relations, (44), the one-electron integrals in Eqs. (83) and (84) nearly always vanish.

3. *Case $L_1 = L_2 = l$*

Setting $L_2 = l-1$ and $L_1 = l$ in Eq. (75) and setting $L_1 = l+1$ and $L_2 = l$ in Eq. (82) we obtain two equations for the integrals $P^{l,l,l}_{N_1,N_2}(\xi_1,\xi_2)$

$$\begin{aligned} & P^{l,l,l}_{N_1,N_2}(\xi_1,\xi_2) + P^{l,l,l}_{N_1,N_2+1}(\xi_1,\xi_2) \\ & \quad = \frac{1}{\xi_2}[(N_1,l,\xi_1|N_2+1,l,\xi_2) - (N_1,l,\xi_1|N_2,l,\xi_2)] \end{aligned} \tag{85}$$

and

$$\begin{aligned} & (N_1+l)P^{l,l,l}_{N_1-1,N_2}(\xi_1,\xi_2) + (N_1-l-1)P^{l,l,l}_{N_1,N_2}(\xi_1,\xi_2) \\ & \quad = \frac{1}{\xi_1}[(N_1+l)(N_1-1,l,\xi_1|N_2,l,\xi_2) \\ & \quad - (N_1-l-1)(N_1-1,l,\xi_1|N_2,l,\xi_2)]. \end{aligned} \tag{86}$$

In the case when $N_1 < N_2$ and $N_1 > l+1$, we use the latter equation, otherwise we use the former one.

V. APPLICATION TO HELIUM

The method for calculation of the one- and two-electron matrix elements described in this paper is general and can be applied to all atoms, or more generally to all one-center integrals. To show that the method really works and can be used to obtain further insights into the atomic structure we apply it to the CI calculation of helium.

A. Algebraic formulation

The Schrödinger equation for the two-electron atoms in atomic units takes the form

$$\left[-\frac{\nabla^2_{(1)}}{2} - \frac{\nabla^2_{(2)}}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}\right]\psi = E\psi, \tag{87}$$

where Z is the charge of the nucleus. In the case of helium we set $Z=2$. By scaling the coordinates of the electrons $\vec{x}^{(i)} \to Z^{-1}\vec{x}^{(i)}$, $i=1,2$, we get an equivalent equation

$$\left[-\frac{\nabla^2_{(1)}}{2} - \frac{\nabla^2_{(2)}}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{Z}\frac{1}{r_{12}}\right]\psi = \frac{E}{Z^2}\psi. \tag{88}$$

Since Hamiltonian in Eq. (88) commutes with the components of the total angular momentum and spin of the electrons, it is advantageous to expand the exact wave function into the symmetry adapted basis functions

$$\begin{aligned} \langle \vec{r}_1,\vec{r}_2|k\rangle = {} & R_{n_{1k},l_{1k}}(r_1\xi_{1k})R_{n_{2k},l_{2k}}(r_2\xi_{2k})\langle \vec{n}_1,\vec{n}_2|(l_{1k},l_{2k}),L,0\rangle \\ & + (-1)^{L+S-l_{1k}-l_{2k}}R_{n_{1k},l_{1k}}(r_2\xi_{1k})R_{n_{2k},l_{2k}}(r_1\xi_{2k}) \\ & \times \langle \vec{n}_2,\vec{n}_1|(l_{1k},l_{2k}),L,0\rangle, \end{aligned} \tag{89}$$

where $R_{n,l}(\xi r)$ are the Sturmian radial function used throughout the paper, $S=0$ refers to the singlets and $S=1$ to the triplets, and finally $|(l_1,l_2),L,0>$ are the eigenstates of the square of the total angular momentum

$$\langle\vec{n}_1,\vec{n}_2|(l_1,l_2),L,0\rangle = \sum_{m=-\min(l_1,l_2)}^{\min(l_1,l_2)} (l_1,m,l_2,\\ -m|L,0)Y_{l_1,m}(\vec{n}_1)Y_{l_2,-m}(\vec{n}_2).$$

Here, $(|)$ denotes the Clebsch-Gordan coefficients.

The calculation of the matrix elements of the operators in Eq. (88) between two functions of the form (89) is reduced either to the calculation of the two-electron integrals (46) or to the calculation of the one-electron integrals. One encounters two kinds of the one-electron integrals. The first one are the overlap integrals that are reduced to the integrals (70)

$$\int d^3r\, R_{n_1,l_1}(\xi_1 r)Y_{l_1,m_1}(\vec{n})R_{n_2,l_2}(\xi_2 r)Y_{l_2,m_2}(\vec{n}) \\ = \sqrt{\frac{(n_1-l_1-1)!}{(n_1+l_1)!}\frac{(n_2-l_1-1)!}{(n_2+l_1)!}}(n_1,l_1,\xi_1|r|n_2,l_1,\xi_2). \tag{90}$$

The second one are the integrals involving the Laplace operator. These are calculated as follows:

$$\int d^3r\, R_{n_1,l_1}(\xi_1 r)Y_{l_1,m_1}(\vec{n})\left(-\frac{\nabla^2}{2}\right)R_{n_2,l_2}(\xi_2 r)Y_{l_2,m_2}(\vec{n}) \\ = \xi_2\int_0^\infty rR_{n_1,l_1}(\xi_1/\xi_2 r)\frac{r}{2}\left(p_r^2+\frac{l_1(l_1+1)}{r^2}\right)R_{n_2,l_1}(r)dr \\ = \sqrt{\frac{(n_1-l_1-1)!}{(n_1+l_1)!}\frac{(n_2-l_1-1)!}{(n_2+l_1)!}}\xi_2(n_1,l_1,\xi_1/\xi_2|T_3/2 \\ +(T_+ + T_-)/4|n_2,l_1,1). \tag{91}$$

Here, we used an expression for the Laplacian operator in spherical coordinates (A8), equation for spherical harmonics (A9), orthonormality of spherical harmonics, and Eqs. (27) and (28). The resulting matrix elements are by means of Eqs. (26) and (30) reduced to the calculation of the overlap integrals (76).

B. Configuration interaction

In this paper we concentrate on calculation of S and P states, i.e., on the states with $L=0$ and $L=1$ in Eq. (89). It follows from properties of Clebsch-Gordan coefficients that for $L=0$ it must be $l_{1k}=l_{2k}=l_k$ and for $L=1$ it must be $l_{1k}=l_{2k}-1=l_k$. Thus, after taking into account all symmetries, we have an infinite number of configurations labeled by set of integers $\{n_{1k},n_{2k},l_k\}$, with k ranged from 1 to infinity. When performing CI calculation we have to truncate this basis set in some manner. Also, we are free to optimize the screening constants ξ_{1k} and ξ_{2k} for different l_k to achieve the rapid convergence of CI method.

In this paper we are mainly interested in the numerical stability of the integrals. The main source of the instabilities are the integrals among highly excited configurations. To know the integrals that have to be evaluated accurately, we need to know the highly excited configurations that contribute significantly. Also, we need to know the values of the screening constants that are close to the optimal ones.

Let us consider the second-order of the perturbation theory

$$E^{(2)} = \sum_{k=1}^{\infty}\frac{W_{k0}^2}{E_0^{(0)}-E_k^{(0)}}. \tag{92}$$

It is seen that if the matrix elements W_{k0} do not vary appreciably with the increasing k, the contributions of the configurations decrease with the increasing unperturbed energies $E_k^{(0} = -(n_{1k}^{-2}+n_{2k}^{-2})/2$. Now it is clear that, for example, $\{1s,(n+1)s\}$ configurations are more significant than $\{2s,(n+2)s\}$ and $\{2p,(n+2)p\}$ configurations. The latter are more significant than $\{3s,(n+3)s\}$, $\{3p,(n+3)p\}$, and $\{3d,(n+3)d\}$ configurations and so on. Generally, for the S states we consider $\{Nl,(N+n)l\}$ configurations with l going from 0 to $N-1$ and with n going from 0 (for the singlets) or from 1 (for the triplets) to some b. For the P states we consider two kinds of configurations: either $\{Nl,(N+n)(l+1)\}$ with l going from 0 to $N-1$ and with n going from 1 to b, or $\{(N+n)l,N(l+1)\}$ with l going from 0 to $N-2$ and with n going from 0 to b.

The question now is how to choose b to pick up the significant configurations. Let us suppose that we have fixed N and l and we are adding to the basis set the states with increasing n. We made variational calculation with k basis functions and calculated the ground state of given symmetry E_k. We add the $(k+1)$th state, obtain E_{k+1} and calculate the difference $E_{k+1}-E_k$. If this difference is less than ε, contribution of the states with fixed N and l is saturated. Addition of the further states with fixed N and l and increasing n does not improve the variational result significantly. For the triplet S and P states we took $\varepsilon=10^{-9}$, for the singlet S state we took $\varepsilon=10^{-7}$. In this way we determined b.

For $\{Ns,(N+n)s\}$ configurations of the triplet S state and $\{1s,np\}$ of the triplet P state we took $\xi_{2k}=1-1/Z$ and $\xi_{1k}=1$. In these configurations, the distinction between the "inner" and "outer" electrons is meaningful. The "inner" electron "sees" the nuclear charge and the "outer" electron "sees" the nuclear charge screened by the "inner" electron. For other configurations we took $\xi_{1k}=\xi_{2k}=1$.

Tables I and II summarize our findings about significant configurations for the S and P states, respectively. For low N the contribution of the states with small $l=0,1,2$ is dominant and we have to take large number of the excitations of the "outer" electron. As we move to larger values of N, the contribution of the states with small l saturates. The dominant contribution is shifted to the states with $l=3,4,5$. Also, as N increases the contributions of the configurations with larger n goes down. In other words, as we are moving to the higher excited states the electrons have tendency to have equal principal quantum numbers.

However, it is seen from Tables I and II that precise dependence of b on N and l that cuts the unsignificant configurations is anything but simple. Perhaps labeling of the configurations by means of the approximate quantum numbers

TABLE I. The basis set used for configuration interaction for the S states. $\{Nl,(N+n)l\}$ configurations are ordered according to the principal quantum number N of the "inner" electron. For fixed N, the orbital quantum number l runs from 0 to $N-1$. For fixed N and l the difference n between the principal quantum numbers of the "outer" and "inner" electron ranges from 0 (for the singlets) or from 1 (for the triplets) to b. b serves to cut the contribution of the states with large n that do not significantly improve the variational result. b was determined from numerical experiments, see the main text for the details.

State	Interval	b
^1S	$N<12,\ l<3$	9
	$N<12,\ l\geq 3$	$9-(l-2)$
	$12\leq N\leq 18$	$6-\lvert l-4\rvert$
^3S	$N\leq 5$	$18-N-2l$
	$6\leq N\leq 8$	$18-N-l$
	$9\leq N\leq 13$	$18-N-\lvert l-4\rvert$

as used by Herrick and Sinanoglu [15] provides the desired "selection rule."

C. Results and discussion

We first discuss accuracy of the eigenvalues and then numerical stability of the integrals. The results presented in Tables III–V show that after relatively fast convergence for small N, the convergence of CI slows down for larger N. The results were compared with those obtained in Ref. [20] with the method of the explicitly correlated functions. As expected, the result for the ground state is not impressive. It is well known that electron-electron correlation for the lowest state of two-electron atoms is very strong. Thus, the results obtained within the orbital method are relatively poor in comparison with those obtained by means of the explicitly correlated functions, see, e.g., Refs. [6,17,21,22]. The latter method has the disadvantage that its extension to the atoms with more than two electrons is very complicated. Three-electron atoms are just on the margin of feasibility [23]. The accuracy of our calculation is much better for the excited states. Our results for 2 ^3S and 2 ^3P states are better than 1 part in 10^6. Considering the simplicity of the basis set used here in comparison with that used in Ref. [20], these results

TABLE II. The same as in Table II but for the P states. The only difference is that in this case we have two kinds of configurations $\{Nl,(N+n)(l+1)\}$ and $\{(N+n)l,N(l+1)\}$.

Configurations	Interval	b
$\{Nl,(N+n)(l+1)\}$	$N=1$	15
	$N=2$	$13-2\lvert l-1\rvert$
	$N=3$	$10-2\lvert l-1\rvert$
	$4\leq N\leq 8,\ l<4$	7
	$4\leq N\leq 8,\ l\geq 4$	$7-(l-3)$
	$9\leq N\leq 13,\ l<7$	4
	$9\leq N\leq 13,\ l\geq 7$	$4-(l-6)$
$\{(N+n)l,N(l+1)\}$	$N=2$	14
	$N=3$	$13-2(l-1)$
	$4\leq N\leq 5$	7
	$6\leq N\leq 10,\ l<4$	5
	$6\leq N\leq 10,\ l\geq 4$	$5-(l-3)$
	$11\leq N\leq 13,\ l<7$	$5-(N-10)$
	$11\leq N\leq 13,\ l\geq 7$	$5-(N-10)-(l-6)$

TABLE III. Variational energy levels E_N of the ground state of helium obtained by diagonalization of the generalized eigenvalue problem (88) for given N. Order denotes the order of the truncated matrix. ΔE denotes the difference E_N-E_{N-1}. The exact value is −2.903724373 [20].

N	Order	E_N	ΔE
1	10	−2.8725067	
2	30	−2.8975136	$-0.25\ 10^{-1}$
3	60	−2.9009036	$-0.33\ 10^{-2}$
4	99	−2.9020298	$-0.11\ 10^{-2}$
5	146	−2.9025655	$-0.53\ 10^{-3}$
6	200	−2.9028682	$-0.30\ 10^{-3}$
7	260	−2.9030582	$-0.18\ 10^{-3}$
8	325	−2.9031862	$-0.12\ 10^{-3}$
9	394	−2.9032773	$-0.91\ 10^{-4}$
10	466	−2.9033447	$-0.67\ 10^{-4}$
11	540	−2.9033962	$-0.51\ 10^{-4}$
12	586	−2.9034357	$-0.39\ 10^{-4}$
13	632	−2.9034672	$-0.31\ 10^{-4}$
14	678	−2.9034922	$-0.24\ 10^{-4}$
15	724	−2.9035120	$-0.19\ 10^{-4}$
16	770	−2.9035277	$-0.15\ 10^{-4}$
17	816	−2.9035404	$-0.12\ 10^{-4}$
18	862	−2.9035508	$-0.10\ 10^{-4}$

TABLE IV. The same as in Table III, but for the 2^3S state. The exact value is −2.175229378 [20].

N	Order	E	ΔE
1	17	−2.174245506	
2	47	−2.175088716	$-0.84\ 10^{-3}$
3	86	−2.175208569	$-0.11\ 10^{-3}$
4	130	−2.175221935	$-0.13\ 10^{-4}$
5	175	−2.175225653	$-0.37\ 10^{-5}$
6	232	−2.175227182	$-0.15\ 10^{-5}$
7	288	−2.175227945	$-0.76\ 10^{-6}$
8	340	−2.175228372	$-0.42\ 10^{-6}$
9	401	−2.175228626	$-0.25\ 10^{-6}$
10	456	−2.175228790	$-0.16\ 10^{-6}$
11	502	−2.175228901	$-0.11\ 10^{-6}$
12	537	−2.175228977	$-0.75\ 10^{-7}$
13	562	−2.175229025	$-0.47\ 10^{-7}$

TABLE V. The same as in Table III, but for the 2^3P state. The exact value is −2.133164181 [20].

N	Order	E	ΔE
1	15	−2.131319860	
2	54	−2.132970321	$-0.16\ 10^{-2}$
3	106	−2.133129547	$-0.15\ 10^{-3}$
4	158	−2.133151474	$-0.21\ 10^{-4}$
5	224	−2.133157958	$-0.64\ 10^{-5}$
6	292	−2.133160583	$-0.26\ 10^{-5}$
7	368	−2.133161872	$-0.12\ 10^{-5}$
8	450	−2.133162588	$-0.71\ 10^{-6}$
9	521	−2.133163013	$-0.42\ 10^{-6}$
10	594	−2.133163291	$-0.27\ 10^{-6}$
11	672	−2.133163480	$-0.18\ 10^{-6}$
12	740	−2.133163610	$-0.12\ 10^{-6}$
13	798	−2.133163699	$-0.89\ 10^{-7}$

are good. Going to the higher excited states, the performance of the orbital method further improves, see, e.g., Ref. [4].

To improve the result achieved here it is necessary to optimize screening constants, classify the configurations according to the scheme proposed by Herrick and Sinanoglu and to extrapolate the results to infinite N. This will be discussed elsewhere.

In Table VI a few values of the repulsion integrals between $\{1s,2p\}$ configuration and the excited configurations are presented. Also presented are a few diagonal matrix elements between the highly excited configurations. These configurations are the last considered configurations for given N. The values of the integrals were calculated in the double precision and then compared with the calculation performed in quadruple precision. It is seen from Table VI that the numerical stability of the method is very high. To conclude, these preliminary results show that the algebraic method developed in this paper is sound.

VI. CONCLUSIONS

In this paper two goals were achieved. First, we have shown that conservation of the Runge-Lenz vector and the commutation relations between components of the Runge-Lenz vector and angular momentum provides recurrence relations for the radial functions of the hydrogen. Second, we have shown that these recurrence relations facilitated the numerical stability of calculations. In particular, the integrals over four radial functions were written as a linear combination of the integrals over two radial functions. Numerically stable recurrence relations for the coefficients of the linear combination were found. The integrals over two radial functions were given through numerically stable recurrence relations. The method was applied to the calculation of $1\ ^1S$, $2\ ^3S$, and $2\ ^3P$ states of helium. The results obtained here are in agreement with the other calculations.

We would like to point out that with the methods developed in this paper the treatment of the radial degrees of freedom is neither more complicated nor less elegant than the treatment of the angular ones. We note that the only analytical tools used in the evaluation of the two electron integrals (46) were the multipole expansion (47) and the integration by parts, Eqs. (63) and (71). In the evaluation of the one-electron integrals we calculated analytically the integrals over nodeless functions (B3). The rest of the calculation was algebraic. In fact, the calculation can be carried out in a completely algebraic way [24]. By means of the recurrence relations derived in Sec. III and Appendix B, we can calculate the matrix r_{12}^2. The matrix elements of r_{12}^{-1} then can be calculated by means of the improved Newton method for square-root of the matrix [25].

Algebraic method for the calculation of the atomic integrals developed in this paper can be extended to the calculation of the oscillator strengths [20,26], Bethe logarithm [21,27] and relativistic effects [28] Since the algebraic method for the calculation of the atomic integrals keeps the numerical instabilities under control, it provides the possibility of further improvement of the atomic calculation in general. Therefore, we believe that it is of some interest.

TABLE VI. Values of the integrals $\langle k|r_{12}^{-1}|j\rangle$ as calculated in the double precision where the states $|k\rangle$ and $|j\rangle$ are the symmetry adapted states given by Eq. (89) for the triplet P states, i.e., for $L=1$ and $S=1$. The results were checked in quadruple precision. Error denotes the difference between the results obtained in double and quadruple precision.

n_{1k}	l_{1k}	ξ_{1k}	n_{2k}	l_{2k}	ξ_{2k}	n_{1j}	l_{1j}	ξ_{1j}	n_{2j}	l_{2j}	ξ_{2j}	$\langle k\|r_{12}^{-1}\|j\rangle$	Error
1	0	1	16	1	1/2	10	7	1	9	8	1	$0.900831851943034\ 10^{-4}$	$-0.19\ 10^{-17}$
1	0	1	16	1	1/2	10	8	1	10	9	1	$-0.2890615746201898\ 10^{-4}$	$0.94\ 10^{-18}$
1	0	1	16	1	1/2	12	9	1	11	10	1	$0.1831898394329932\ 10^{-4}$	$-0.16\ 10^{-17}$
1	0	1	16	1	1/2	12	9	1	12	10	1	$0.4890330421218360\ 10^{-4}$	$-0.38\ 10^{-17}$
1	0	1	16	1	1/2	13	8	1	13	9	1	$0.1977285617128401\ 10^{-3}$	$-0.68\ 10^{-17}$
10	7	1	9	8	1	10	7	1	9	8	1	17.00271743870608	$-0.11\ 10^{-13}$
10	8	1	10	9	1	10	8	1	10	9	1	19.73464697927070	$0.19\ 10^{-13}$
12	9	1	11	10	1	12	9	1	11	10	1	21.51748282351638	$-0.12\ 10^{-13}$
12	9	1	12	10	1	12	9	1	12	10	1	22.41407884446250	$-0.20\ 10^{-14}$
13	8	1	13	9	1	13	8	1	13	9	1	21.84661070151542	$066\ 10^{-14}$

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APPENDIX A

This appendix is divided into four subsections. Decomposition of the operators into the radial and angular parts is described and the algebra of the angular operators is treated. The most important results on the angular momentum are summarized. The selection rules and the calculation of nonzero matrix elements of the class of the vector operators between spherical harmonics are given. The class of the vector operators considered here is a special case of the so(3) vector operators, see, e.g., Refs. [13,29,30]. In the exposition of the representation theory of so(3) vector operators we proceed along the lines of the paper [13], though some details are different.

1. Algebra of the angular operators

Taking the dot product of $\vec{n}$ and ∇^n, we get from Eqs. (4) and (6) that

$$n_k\nabla^n_k = 0. \tag{A1}$$

The ordering in the last equation is important, since components of $\vec{n}$ and ∇^n do not commute. To get their commutation relations, let us consider the well-known commutation relation $[\nabla_j,x_k]=\delta_{jk}$ and insert Eqs. (5) and (3) into ∇_j and x_k, respectively. After simple manipulations we obtain

$$[\nabla^n_j,n_k] = \delta_{jk} - n_j n_k. \tag{A2}$$

Setting $j=k$, we get (recalling that Einstein summation convention is used)

$$[\nabla^n_k,n_k] = 2. \tag{A3}$$

Equation (A1) yields an even stronger result, namely,

$$\nabla^n_k n_k = 2. \tag{A4}$$

Further, using Eqs. (3) and (5) we obtain for the components of the angular momentum

$$L_j = -i\varepsilon_{jkl}x_k\nabla_l = -i\varepsilon_{jkl}rn_k\left(n_l\frac{\partial}{\partial r} + \frac{\nabla^n_l}{r}\right) = -i\varepsilon_{jkl}n_k\nabla^n_l. \tag{A5}$$

Here, we used the well-known theorem that the product of a symmetric tensor and an antisymmetric tensor vanishes. From the last equation it is immediately clear that the components of $\vec{L}$ depend on the angular variables only. Further, taking the dot product of the vector operator $\vec{L}$ with itself we obtain

$$L^2 = -(\nabla^n)^2. \tag{A6}$$

Here, we used Eqs. (A1), (A2), and (A4) and the identity

$$\varepsilon_{jkl}\varepsilon_{jpq} = \delta_{kp}\delta_{lq} - \delta_{kq}\delta_{lp}. \tag{A7}$$

The expression for the Laplace operator in spherical coordinates can be easily obtained from Eqs. (5), (A1), (A4), and (A6)

$$-\nabla^2 = p_r^2 + \frac{L^2}{r^2}. \tag{A8}$$

Also, it immediately follows that the Hamiltonian H in Eq. (1) commutes with the square and the third component of the angular momentum L^2 and L_3.

2. Angular momentum

Let us recall only some very important relations derived in the algebraic treatment of the angular momentum. The eigenvalues and eigenvectors of the square of angular momentum and one of its components are defined by equations

$$L^2|l,m\rangle = l(l+1)|l,m\rangle \tag{A9}$$

and

$$L_3|l,m\rangle = m|l,m\rangle. \tag{A10}$$

It is advantageous to introduce the step-up and step-down operators $L_\pm = L_1 \pm iL_2$. One can show that these operators act on the eigenstates $|l,m\rangle$ as follows:

$$L_\pm|l,m\rangle = \sqrt{(l\mp m)(l+1\pm m)}|l,m\pm 1\rangle. \tag{A11}$$

Taking the Hermitian conjugate of this equation we obtain

$$\langle l,m|L_\mp = \langle l,m\pm 1|\sqrt{(l\mp m)(l+1\pm m)}. \tag{A12}$$

The magnetic quantum number m runs from $-l$ to l by 1. For orbital motion, the values of m have to be integers. Hence, possible values of orbital quantum number l are non-negative integers. The projections of the eigenvectors $|l,m\rangle$ into the coordinate basis are called spherical harmonics $Y_{l,m}(\theta,\varphi) = \langle\vec{n}|l,m\rangle$.

3. Selection rules

Next we show that from the commutation relations of the vector operators $\vec{n}$ and ∇^n with the components of the angular momentum $\vec{L}$ we can determine the matrix elements of these operators between the spherical harmonics. To get the selection rules for the quantum number l we begin by noticing that the components of operator ∇^n_k do not mutually commute. To see this, we start from the commutation relation $[\nabla_j,\nabla_k]=0$ and insert the decomposition (5) into ∇_k. Using Eq. (A2), we obtain after some manipulations

$$[\nabla^n_k,\nabla^n_j] = n_k\nabla^n_j - n_j\nabla^n_k. \tag{A13}$$

Using this equation together with Eqs. (A2) and (A6) we derive the commutation relations

$$[L^2,n_k] = 2(n_k - \nabla^n_k) \tag{A14}$$

and

$$[L^2,\nabla_k^n] = -2n_k L^2. \tag{A15}$$

The last two equations are operator identities. Multiplying these equations from the left by $\langle l',m'|$ and from the right by $|l,m\rangle$ and using Eq. (A9), we obtain after simple manipulations two very important equations, namely,

$$\langle l',m'|\nabla_k^n|l,m\rangle = \frac{2+l(l+1)-l'(l'+1)}{2}\langle l',m'|n_k|l,m\rangle \tag{A16}$$

and

$$(l'+l+2)(l'+l)(l'+1-l)(l'-1-l)\langle l',m'|n_k|l,m\rangle = 0. \tag{A17}$$

It follows from these two equations that the matrix elements of operators $\vec{n}$ and ∇^n among spherical harmonics vanish whenever $l' \neq l\pm 1$.

Let us now find the selection rules for the quantum number m. We start with the observation that for every vector operator $\vec{V}$ of the form (12) the commutation relations

$$[L_j,V_k] = i\varepsilon_{jkm}V_m \tag{A18}$$

holds. This follows from Eqs. (A2), (A5), and (A13). Thus, the operators $\vec{V}$ given by Eq. (12), are special cases of the so(3) vector operators, see, e.g., [13,29,30]. It follows from these equations that

$$[L_3,V_3] = 0 \tag{A19}$$

and

$$[L_3,V_\pm] = \pm V_\pm, \tag{A20}$$

where the usual notation

$$V_\pm = V_1 \pm iV_2 \tag{A21}$$

has been used. Multiplying the last two equations by $\langle l'm'|$ from the left and by $|l,m\rangle$ from the right and using Eq. (A10) we get

$$\langle l',m'|V_3|l,m\rangle = 0, m' \neq m \tag{A22}$$

and

$$\langle l',m'|V_\pm|l,m\rangle = 0, m' \neq m \pm 1. \tag{A23}$$

4. Calculation of nonzero matrix elements

The nonzero matrix elements of operator $\vec{V}$ can be evaluated by means of the commutator

$$[L_+,V_+] = 0. \tag{A24}$$

This equation follows from Eq. (A18). Further, we multiply this equation by $\langle l-1,m+1|$ from the left and by $|l,m\rangle$ from the right. Using Eqs. (A11) and (A12) to get the action of operator L_+ on spherical harmonics, we obtain

$$\frac{\langle l-1,m+1|V_+|l,m\rangle}{\langle l-1,m+2|V_+|l,m+1\rangle} = \sqrt{\frac{(l-m)(l-m-1)}{(l-m-1)(l-m-2)}}. \tag{A25}$$

Since the numerator and denominator on both sides of this equation differ by the substitution $m\to m+1$, the most general form of the matrix elements reads

$$\langle l-1,m+1|V_+|l,m\rangle = c_l\sqrt{(l-m)(l-1-m)}, \tag{A26}$$

where coefficient c_l is independent on m.

The matrix elements of operators V_3 and V_- can now easily be found. Using the last equation, the commutation relation

$$V_3 = -\frac{1}{2}[L_-,V_+] \tag{A27}$$

and Eqs. (A11) and (A12) we obtain the matrix element of operator V_3

$$\langle l-1,m|V_3|l,m\rangle = c_l\sqrt{(l-m)(l+m)}. \tag{A28}$$

Similarly, using the last equation, Eqs. (A11) and (A12) and the commutation relation

$$V_- = [L_-,V_3], \tag{A29}$$

we finally obtain

$$\langle l-1,m-1|V_-|l,m\rangle = -c_l\sqrt{(l+m-1)(l+m)}. \tag{A30}$$

The remaining nonzero matrix elements can be obtained by assuming that operator V_3 is real. Coefficient c_l is then real. Taking the Hermitian conjugate of Eqs. (A26), (A28), and (A30), we get successively

$$\langle l+1,m-1|V_-|l,m\rangle = c_{l+1}\sqrt{(l-m+2)(l-m+1)}, \tag{A31}$$

$$\langle l+1,m|V_3|l,m\rangle = c_{l+1}\sqrt{(l+1-m)(l+1+m)}, \tag{A32}$$

and

$$\langle l+1,m+1|V_+|l,m\rangle = -c_{l+1}\sqrt{(l+m+1)(l+m+2)}. \tag{A33}$$

So far, we have determined dependence of the matrix elements on the quantum number m. To determine coefficient c_l, we note that

$$\begin{aligned}(V_+V_- + V_3^2)|l,m\rangle &= [c_l^2(2l-1)(l+m) + c_{l+1}^2(l+1-m)(2l+3)]|l,m\rangle \\ &= (V^2 - i[V_1,V_2])|l,m\rangle.\end{aligned} \tag{A34}$$

The first equality follows from Eqs. (A26), (A28), and (A30)–(A33). The second equality follows from Eq. (A21) and the definition of $V^2 = V_kV_k$. Equation (A34) is an important result and it was used in the Sec. II to determine spectrum of the hydrogen atom.

APPENDIX B

In Sec. IV we showed that calculation of two-electron integrals can be reduced to calculation of one-electron integrals (76). Algebraic calculation of the overlap integrals (76) is described in this appendix. We first calculate integrals $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)$ for $L_1=L_2$. Knowing these integrals, we calculate the integrals with $L_1\neq L_2$. Again, it is important to calculate these integrals in a numerically stable way. The results obtained in this subsection can also be obtained by analytical method, see, e.g., Ref. [31].

1. Case $N_2=L_2+1$ and $L_1=L_2$

Considering Eq. (85) for $N_2=l$ yields

$$P^{l,l,l}_{N_1,l+1}(\xi_1,\xi_2)=\frac{1}{\xi_2}(N_1,l,\xi_1|l+1,l,\xi_2). \tag{B1}$$

Inserting this equation into Eq. (86) for $N_2=l+1$ we obtain the formula

$$(N_1+1,l,\xi_1|l+1,l,\xi_2)=\frac{N_1+l+1}{N_1-l}\frac{\xi_2-\xi_1}{\xi_2+\xi_1}(N_1,l,\xi_1|l+1,l,\xi_2). \tag{B2}$$

This equation is solved with the initial condition

$$(l+1,l,\xi_1|l+1,l,\xi_2)=(2^2\xi_1\xi_2)^{l+1}\frac{(2l+1)!}{(\xi_1+\xi_2)^{2l+2}}. \tag{B3}$$

This equation is obtained by inserting Eqs. (45) and (62) into Eq. (76). Having established this formula we need only to raise the quantum number N_2 from the value $l+1$ to an arbitrary value and to raise the quantum number L_2 from the value l.

2. Case $L_1=L_2$

To raise the quantum number N_2 from the value $l+1$ to an arbitrary value we start with the "analytic" formula

$$\begin{aligned}\int_0^\infty r\left(\frac{d}{dr}+\frac{1}{r}\right)&[r\tilde{R}_{N_1,L_1}(\xi_1r)\tilde{R}_{N_2,L_2}(\xi_2r)]dr\\ &=0=\int_0^\infty r\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)\tilde{R}_{N_1,L_1}(\xi_1r)\right]\tilde{R}_{N_2,L_2}(\xi_2r)dr\\ &\quad+\int_0^\infty r\left[r\left(\frac{d}{dr}+\frac{1}{r}\right)\tilde{R}_{N_2,L_2}(\xi_2r)\right]\tilde{R}_{N_1,L_1}(\xi_1r)dr.\end{aligned} \tag{B4}$$

Applying Eq. (64) we obtain

$$\begin{aligned}(N_1-L_1)&(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &-(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &+(N_2-L_2)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_2)\\ &-(N_2+L_2)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2)=0.\end{aligned} \tag{B5}$$

Further, we consider expression

$$\int_0^\infty r2r\tilde{R}_{N_1,L_1}(\xi_1r)\tilde{R}_{N_2,L_2}(\xi_2r)dr$$

and let $2r$ act first on the function $\tilde{R}_{N_1,L_1}(\xi_1r)$, second on the function $\tilde{R}_{N_2,L_2}(\xi_2r)$. Operator $2r$ acts on these functions according to Eq. (78) as

$$\begin{aligned}\int_0^\infty r2r&\tilde{R}_{N_1,L_1}(\xi_1r)\tilde{R}_{N_2,L_2}(\xi_2r)\\ &=\frac{1}{\xi_1}[2N_1(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad-(N_1-L_1)(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad-(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)]\\ &=\frac{1}{\xi_2}[2N_2(N_1,L_1,\xi_1|N_2,L_2,\xi_2)-(N_2-L_2)(N_1,L_1,\xi_1|N_2\\ &\quad+1,L_2,\xi_2)-(N_2+L_2)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2)].\end{aligned} \tag{B6}$$

Eliminating $(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)$ from one of the Eqs. (B5) and (B6) we obtain

$$\begin{aligned}(N_2-L_2)&\left(\frac{1}{\xi_1}+\frac{1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_2)\\ &=2\left(-\frac{N_1}{\xi_1}+\frac{N_2}{\xi_2}\right)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &\quad+(N_2+L_2)\left(\frac{1}{\xi_1}-\frac{1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2)\\ &\quad+2\frac{N_1+L_1}{\xi_1}(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2).\end{aligned} \tag{B7}$$

Using this equation for $L_1=L_2=l$ together with Eq. (B2) we obtain all possible integrals $(N_1,l,\xi_1|N_2,l,\xi_2)$.

3. Case $L_1\neq L_2$

In general, we can assume that $L_1<L_2$, since obviously $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)=(N_2,L_2,\xi_2|N_1,L_1,\xi_1)$. We raise quantum number L_2 from the value $L_2=L_1$ to the needed value as follows.

For the action of operator $r(\frac{d}{dr}+\frac{1}{r})$ on the function $\tilde{R}_{N_2,L_2}(\xi_2r)$ in Eq. (B4) we use Eq. (65) instead of Eq. (64). We obtain

$$\begin{aligned}(N_1-L_1)&(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &-(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)\\ &+(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)\\ &-(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)\\ &+2(L_2+1)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)=0.\end{aligned} \tag{B8}$$

Further, for the action of operator $2r$ on the function $\tilde{R}_{N_2,L_2}(\xi_2r)$ in Eq. (B6) we use Eq. (77) instead of Eq. (78). We get

$$
\begin{aligned}
&\frac{1}{\xi_1}[2N_1(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\
&\quad-(N_1-L_1)(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)\\
&\quad-(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)]\\
&\quad=\frac{1}{\xi_2}[-2(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)\\
&\qquad+(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)\\
&\qquad+(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)]. \qquad (B9)
\end{aligned}
$$

Eliminating integrals $(N_1+1,L_1,\xi_1|N_2,L_2,\xi_2)$ from one of the Eqs. (B8) and (B9) we obtain

$$
\begin{aligned}
&2(N_1+L_2+1)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\
&\quad=2(N_1+L_1)(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)\\
&\qquad-\left(1-\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)\\
&\qquad-2\frac{\xi_1}{\xi_2}(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)\\
&\qquad+\left(1+\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2). \qquad (B10)
\end{aligned}
$$

This equation could be used for calculating the integrals $(N_1,L_1,\xi_1|N_2,L_2,\xi_2)$ as it stands. However, it turns out that it is more advantageous to combine the last equation with Eq. (B7). Elimination of the integrals $(N_1-1,L_1,\xi_1|N_2,L_2,\xi_2)$ from one of these equations yields

$$
\begin{aligned}
&\left(1+\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_2)\\
&\quad-2\frac{\xi_1}{\xi_2}(N_1,L_1,\xi_1|N_2,L_2+1,\xi_2)\\
&\quad-\left(1-\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2+1,\xi_2)\\
&\quad=2\left(N_2\frac{\xi_1}{\xi_2}+L_2+1\right)(N_1,L_1,\xi_1|N_2,L_2,\xi_2)\\
&\qquad-(N_2-L_2)\left(1+\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_2)\\
&\qquad+(N_2+L_2)\left(1-\frac{\xi_1}{\xi_2}\right)(N_1,L_1,\xi_1|N_2-1,L_2,\xi_2). \qquad (B11)
\end{aligned}
$$

We run this equation starting from $L_2=L_1$ successively ascending the quantum number L_2 to the desired value. In particular, considering the last equation for $\xi_1=\xi_2$ leads to the equation

$$
\begin{aligned}
&(N_1,L_1,\xi_1|N_2+1,L_2+1,\xi_1)-(N_1,L_1,\xi_1|N_2,L_2+1,\xi_1)\\
&\quad=(N_2+L_2+1)(N_1,L_1,\xi_1|N_2,L_2,\xi_1)\\
&\qquad-(N_2-L_2)(N_1,L_1,\xi_1|N_2+1,L_2,\xi_1). \qquad (B12)
\end{aligned}
$$

Taking into account the orthogonality of the radial functions for the same ξ, Eq. (44), we get that integrals $(N_1,L_1,\xi|N_2,L_2,\xi)$ vanish for $L_1<L_2$ and $N_1>N_2$. The nonzero integrals can be easily calculated from the last equation starting with $N_1=N_2+1$ and $L_1=L_2$.

4. Generalizations

We would like to remark that the algebraic method developed so far can also be applied to the evaluation of integrals $\int_0^\infty r^{p+1}R_{n_1,l_1}(\xi_1 r)R_{n_2,l_2}(\xi_2 r)dr$, for both positive and negative p (see also Refs. [12,32,33]). If p is positive, we use one of Eqs. (31), (35), and (36) to reduce the integrals to the form (76). If p is negative, we consider Eq. (31), Eq. (35) with l replaced by $l-1$ and Eq. (36) with l replaced by $l+1$. We eliminate $R_{n+1,l}(\xi r)$ and $R_{n-1,l}(\xi r)$ from these equations and get

$$
\begin{aligned}
r^{-1}R_{n,l}(\xi r)=&\frac{\xi}{l(l+1)(2l+1)}[l\sqrt{(n+l+1)(n-l-1)}\\
&\times R_{n,l+1}(\xi r)+(l+1)\sqrt{(n+l)(n-l)}\\
&\times R_{n,l-1}(\xi r)+(2l+1)nR_{n,l}(\xi r)]. \qquad (B13)
\end{aligned}
$$

By means of this equation we reduce the integrals of the form $\int_0^\infty r^{-|p|+1}R_{n_1,l_1}(\xi_1 r)R_{n_2,l_2}(\xi_2 r)dr$ to the integrals of the form (76).

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