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Coupled Hartree-Fock method for calculating Sternheimer shielding

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We have extended our calculations of Sternheimer shielding functions of Ref. 1 by introducing exchange terms via the self-consistent Hartree-Fock perturbation method. This procedure becomes relatively time consuming. It takes for Pr^{3+} 2-1/2 h of CPU time at a TR 440 computer to achieve convergency after 10 iterations. In addition to the acccurate method we have also studied an approximate version, which handles the calculation of exchange integrals in a simplified form so as to make the computational procedure very fast. The approximations inherent to this procedure, however, yield unreliable results, unless the wave functions are considerably contracted. Our results from the accurate method are compared with values reported in the literature, which also take consistency, exchange, and correlation effects into account. We conclude from our study that consistency effects in deriving Sternheimer corrections are dominant over correlation effects.

I. INTRODUCTION

We have been motivated to calculate Sternheimer shielding functions $\gamma(r)$ by our work on the molecular-orbital (MO) interpretation of experimental quadrupole splittings. In MO or band calculations, which include only valence orbitals within the MO basis set, the electron core of the isotope under study becomes polarized by valence electrons, by overlap, or by ligand charges. The amount of polarization depends on $\gamma(r)$ and accounts for shielding $[\gamma(r)>0]$ or antishielding $[\gamma(r)<0]$ effects in deriving the quadrupole coupling constant.

Recently (Paper I, Ref. 1) we have calculated Sternheimer shielding functions $\gamma(r)$ for various elements (Li, Na, K, Rb, F, Cl, Br, I, Cu, Fe, Ag, Pr) using Sternheimer's non-self-consistent and self-consistent procedure.[2] Sternheimer's self-consistent theory takes care of Coulomb interaction between the perturbed core orbitals but neglects exchange interaction. To take the exchange interaction into account we introduced in Paper I the $X\alpha$-exchange potential and performed self-consistent calculations. However, we were not able to derive satisfactory results. Alternative calculational procedures, which include exchange and which are self-consistent, are the coupled-Hartree-Fock method (CHFM),[3-6] the linked-cluster-many-body perturbation theory (LCMBPT),[7-9] and the differential-equation method (DEPM), which treats consistency as a perturbation.[10] The LCMBP theory is superior to CHFM and DEPM in the sense that it includes correlation effects, while CHFM neglects correlation contributions partly, and DEPM neglects them completely. However, LCMBPT is based on total energy calculations, thus making the evaluation of $\gamma(r)$ (instead of γ_∞) not straightforward. We followed therefore the CHF method here, but restricted ourselves to closed-shell systems.

II. THEORY

The CHF method is based on the self-consistent solution of the first-order perturbed Schrödinger equation[6]

$$\left(-\vec{\nabla}_j^2-\frac{2Z}{r}+2\sum_{k=1}^{N}\int\frac{|\psi_{0,k}(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\,d^3r-E_{0,j}\right)\psi_{1,j}(\vec{r})$$

$$=2\sum_{k=1}^{N}\|\int\frac{\psi_{0,k}(\vec{r}\,')\psi_{1,j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{0,k}(\vec{r})-\left(H_{1,j}-E_{1,j}+4\sum_{k=1}^{N}\int\frac{\psi_{1,k}(\vec{r}\,')\psi_{0,k}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\right)\psi_{0,j}(\vec{r})$$

$$+2\sum_{k=1}^{N}\|\left(\int\frac{\psi_{0,k}(\vec{r}\,')\psi_{0,j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{1,k}(\vec{r})+\int\frac{\psi_{1,k}(\vec{r}\,')\psi_{0,j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{0,k}(\vec{r})\right),\qquad(1)$$

where wave functions $\psi_j(\vec{r})$ consist of the unperturbed part $\psi_{0,j}(\vec{r})$ and the perturbed part $\psi_{1,j}(\vec{r})$:

$$\psi_j(\vec{r})=\psi_{0,j}(\vec{r})+\psi_{1,j}(\vec{r}).$$

The symbol $\sum \|$ in Eq. (1) represents the summation over electrons with parallel spin only. $H_{1,j}$ is the one-particle perturbation operator[1] acting on particle j, and $E_{1,j}$ defines the perturbed energy in 1st order for the jth orbital. The unperturbed orbitals $\psi_{0,j}(\vec{r})$ are the solution of the HF equations

$$\left(-\vec{\nabla}_j^2-\frac{2Z}{r}\right)\psi_{0,j}(\vec{r})+2\sum_{k=1}^{N}\int\frac{|\psi_{0,k}(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{0,j}(\vec{r})-2\sum_{k=1}^{N}\|\int\frac{\psi_{0,k}(\vec{r}\,')\,\psi_{0,j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{0,k}(\vec{r})=E_{0,j}\,\psi_{0,j}(\vec{r})\,. \tag{2}$$

We substitute the unperturbed energy $E_{0,j}$ and the potential $2Z/r$ in Eq. (1) by means of the unperturbed Eq. (2) and separate the angular and radial part of the perturbed and unperturbed wave functions according to

$$\psi_{0,j}(\vec{r})=\frac{u_{nl}^{(0)}(r)}{r}Y_m^l(\theta,\varphi)\,,$$

$$\psi_{0,k}(\vec{r})=\frac{u_{n_1l_1}^{(0)}(r)}{r}Y_m^{l_1}(\theta,\varphi)\,,$$

$$\psi_{1,j}(\vec{r})=\frac{u_{nl'}^{(1)}(r)}{r}Q\langle Y_m^{l'}(\theta,\varphi)|C_0^2|Y_m^l(\theta,\varphi)\rangle Y_m^{l'}(\theta,\varphi)\,,$$

$$\psi_{1,k}(\vec{r})=\frac{u_{n_1l_1}^{(1)}(r)}{r}Q\langle Y_m^{l_1'}(\theta,\varphi)|C_0^2|Y_m^{l_1}(\theta,\varphi)\rangle Y_m^{l_1'}(\theta,\varphi)\,.$$

Multiplication of Eq. (1) with the angular part of $\psi_{1,j}(\vec{r})$ and integration over the angles θ and φ leads to the following equation,[11] the self-consistent solution of which yields the perturbed orbitals $u_{nl'}(r)$:

$$\begin{aligned}\left(-\frac{\partial^2}{\partial r^2}+\frac{1}{u_{nl}^{(0)}(r)}\frac{\partial^2 u_{nl}^{(0)}(r)}{\partial r^2}+\frac{(l'-l)(l'+l+1)}{r^2}+2\sum_{n_1,l_1,L}(C_3-C_1)Z_1(r)+2\sum_{n_1,l_1,L}\|C_2Z_2(r)\frac{u_{n_1l_1}^{(0)}(r)}{u_{nl}^{(0)}(r)}\right)u_{nl'}^{(1)}(r)\\ =u_{nl}^{(0)}(r)\left(r^{-3}+E_{1,n}\delta_{ll'}-4\sum_{n_1,l_1,l_1',L}C_5Z_5(r)\right)+2\sum_{n_1,l_1,l_1',L}\|[C_6Z_6(r)u_{n_1l_1'}^{(1)}(r)+C_7Z_7(r)u_{n_1l_1}^{(0)}(r)]\\ +2\sum_{n_1,l_1,L}\|C_4Z_4(r)u_{n_1l_1}^{(0)}(r)\,,\end{aligned} \tag{3}$$

with

$$E_{1,n}=-\langle u_{nl}^{(0)}(r)|r^{-3}|u_{nl}^{(0)}(r)\rangle+4\sum_{n_1,l_1,l_1',L}C_8Z_8-4\sum_{n_1,l_1,l_1',L}\|C_9Z_9\,. \tag{4}$$

The coefficients C_i resulting from the angular integrations and radial integrals Z_i are derived in the Appendix. The general method of solving Eq. (3) was originally derived by Sternheimer (see Refs. 2 and 29 of Paper I).

Since the computational time and the memory space required for the solution of Eq. (3) (especially for heavy elements from transition elements on) is exorbitantly high, we introduced the following approximations:

$$\int\frac{\psi_{0,k}(\vec{r}\,')\psi_{1,k}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{0,k}(\vec{r})=\frac{\psi_{0,k}(\vec{r})}{\psi_{0,j}(\vec{r})}\int\frac{\psi_{0,k}(\vec{r}\,')\,\psi_{0,j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{1,j}(\vec{r})\,, \tag{5}$$

$$\int\frac{\psi_{1,k}(\vec{r}\,')\,\psi_{0,j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{0,k}(\vec{r})=\int\frac{\psi_{0,k}(\vec{r}\,')\,\psi_{0,j}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\,\psi_{1,k}(\vec{r})\,. \tag{6}$$

Approximation (5) was already described and used by Khubchandani *et al.*[12] The advantage of both approximations is (i) that the perturbed energy remains invariant under the application of Eqs. (5) and (6), and (ii) that memory space and computer time are reduced at least by a factor of 4 for each iteration. With these approximations we get instead of Eq. (3) the simplified form for the first-order perturbed Schrödinger equation. In the present study we have applied these approximations to closed-shell systems:

$$\begin{aligned}\left(-\frac{\partial^2}{\partial r^2}+\frac{1}{u_{nl}^{(0)}(r)}\frac{\partial^2 u_{nl}^{(0)}(r)}{\partial r^2}+\frac{(l'-l)(l'+l+1)}{r^2}\right)u_{nl'}^{(1)}(r)\\ =\left(r^{-3}+E_{1,n}\delta_{ll'}-4\sum_{n_1,l_1,l_1',L}C_5Z_5(r)\right)u_{nl}^{(0)}(r)\\ +4\sum_{n_1,l_1,l_1',L}C_6Z_6(r)u_{n_1l_1'}^{(1)}(r)\,,\end{aligned} \tag{7}$$

where $E_{1,n}$ is given by Eq. (4).

With the self-consistent solution $u_{nl}^{(1)}(r)$ of Eq. (5) or Eq. (7), respectively, we derive the Stern-

TABLE I. γ_∞ values for various atoms and ions.

Atom/ion	Non-self-consistent Sternheimer procedure (Ref. 1)	Self-consistent Sternheimer procedure (Ref. 1)	CHF method (present work)[a]	Unperturbed wave functions	Literature values	Method	Reference	Unperturbed wave function
Be^0	1.01		0.77(0.18)	HF(Clementi[b])	1.02	AE-CHF	15	HF(Clementi[c])
B$^+$	0.71		0.54(0.28)	HF(Clementi[b])	0.82	AE-CHF	15	HF(Clementi[c])
Na$^+$	−4.64	−3.92	−7.09(−4.10)	HF(Clementi[b])	−3.81	LCMBPT	7	?
					−5.72	AE-CHF	16	HF(Clementi[c])
K$^+$	−17.74	−15.02	−28.26(−14.80)	HF(Clementi[b])	−18.27	AE-CHF	17	HF(Clementi[c])
F$^-$	−22.32	−16.97	diverges(−16.48)	HF(Clementi[b])	−29.88	AE-CHF	16	HF(Clementi[c])
					−19.29	DEPM	10	?
Cl$^-$	−55.35	−44.33	diverges(−46.82)	HF(Clementi[b])	−63.21	AE-CHF	17	HF(Clementi[c])
	−69.47		diverges(−56.77)	HF(Watson *et al.*[d])	−56.58	DEPM	10	HF(Watson *et al.*[d])
Br$^-$	−132.60	−108.40	diverges(−112.86)	HF(Clementi[b])				
	−124.70		diverges(−104.79)	HF(Watson *et al.*[d])	−130.20	DEPM	10	HF(Watson *et al.*[d])
I$^-$	−253.80	−209.00	diverges(−225.27)	HF(Clementi[b])				
Ar^0	−26.66		diverges(−23.64)	HF(Clementi[b])	−26.62	AE-CHF	17	HF(Clementi[c])
	−29.84		diverges(−25.20)	HF(Watson *et al.*[d])	−26.71	AE-CHF	18	HF(Clementi[e])
Cu$^+$	−16.04	−5.38	−13.08(−13.61)	HF(Clementi[b])				
Rb$^+$	−47.61	−39.81	−79.12(−42.13)	HF(Clementi[b])				
	−47.20		−78.58(−42.50)	HF(Watson *et al.*[d])	−46.60	DEPM	8	HF(Watson *et al.*[d])
Ag$^+$	−34.20	−18.66	−27.54(−29.38)	HF(Clementi[b])				
Sn^{2+}	−20.75		not calc(−20.02)	HF(Clementi[b])				
Pr^{3+}	−56.51	−57.95	−65.91(−54.11)	HF(Clementi[b])	−142.12	LCMBPT	9,25	HFS(functions[f])

[a] Values without and with brackets obtained from Eq. (3) and Eq. (7), respectively.

[b] Reference 24.

[c] Reference 25.

[d] Reference 26.

[e] Reference 27.

[f] Reference 20.

heimer shielding function $\gamma(r)$ using relation[2]:

$$\gamma(r)=\sum_{n}\sum_{ll'}\frac{C_{ll'}}{Q}\left(\int_0^r u_{nl}^{(0)}(r')u_{nl'}^{(1)}(r')r'^2\,dr' + r^5\int_r^\infty r'^{-3}u_{nl}^{(0)}(r')u_{nl'}^{(1)}(r')\,dr'\right),$$

where $C_{ll'}$ is defined as[2]

$$C_{ll'}=8\sum_{m=-l}^{l}\left[\langle Y_m^{l'}(\theta,\varphi)\,|\,C_0^2\,|\,Y_m^l(\theta,\varphi)\rangle\right]^2 .$$

Unlike our earlier calculations[1] where we used a mesh of the radial integration interval with 720 up to 1440 points to get reliable accuracy, we introduced here numerical procedures with higher accuracy (9 point integration—and differentiation formulas instead of 5 point differentiation—and 7 point integration formulas). Furthermore, we converted all integral functions according to a procedure, described by Hartree,[13] which avoids a good deal of numerical integration. Thus we were able to decrease the number of points to 201. Details of the numerical procedure are described elsewhere.[11]

III. RESULTS AND DISCUSSION

With the theory described in Sec. II we calculated $\gamma(r)$ for the closed-shell systems Be^0, B^+, F^-, Cl^-, Br^-, I^-, Na^+, K^+, Rb^+, Cu^+, Ag^+, Sn^{2+}, and Pr^{3+} (neglecting $4f$ electrons). With respect to MO calculations[14] including Mossbauer or nuclear quadrupole resonance (NQR) isotopes, we also derived $\gamma(r)$ for atoms and ions excluding valence orbitals (F^-, Cl^-, Br^-, I^-, K^+, Zn^{2+}, Sn^{2+}, Te^0, Fe^0, Fe^{2+}, Fe^{3+}). The corresponding asymptotic values γ_∞ are summarized in Tables I and II.

For F^-, Cl^-, Br^-, I^-, and Ar^0 the accurate CHF version was divergent. We therefore also tried a relation for the perturbed orbitals within the iterative scheme, which avoids minimum damping,

$$\tilde{u}_{nl'}^{p}(r)=u_{nl'}^{p-1}(r)+\lambda\left[u_{nl'}^{p}(r)-u_{nl'}^{p-1}(r)\right].$$

Varying λ between 1 (minimum damping) and 0.6, however, only affects the computation time but does not change the convergence (or divergence) behavior itself.

Although the approximate CHF version achieves convergency throughout and requires much less CPU time (about $\frac{1}{4}$ in average) and memory space than the accurate version, the approximations inherent to Eqs. (5) and (6) seem to be too crude to yield reliable results. The deviations of the approximate from the accurate results are largest if the outermost shell has p^6 configuration (Na^+, K^+, Rb^+) because the largest absolute contributions to $\gamma(r)$ are due to the radial excitations of p electrons. In case the outermost shell has an s^2 configuration (Be^0, B^+, Pr^{3+}—$4f^2$ neglected) these deviations are smaller, because s electrons contribute to $\gamma(r)$ only through relatively small angular excitations. Only if the outermost shell has d^{10} configuration (Cu^+, Ag^+) or if the valence electrons are removed totally from the calculation

TABLE II. γ_∞ values for various ions and atoms, derived by excluding valence electrons from the calculations. (These γ_∞ values may be used for core corrections of electric field gradients, which are derived from molecular orbital calculations with a limited basis set, i.e., with valence orbitals.)

Atom/ion	Non-self-consistent Sternheimer procedure	Self-consistent Sternheimer procedure	CHF method (present work)	Calculation performed excluding valence electrons	
Cl^0	−1.23	−1.12		$3s^2$	$3p^5$
Br^0	−6.22	−5.01		$4s^2$	$4p^5$
I^0	−13.10	−13.40		$5s^2$	$5p^5$
F^-	0.08		0.08	$2s^2$	$2p^6$
Cl^-	−1.21	−1.10	−1.15	$3s^2$	$3p^6$
Br^-	−6.09	−4.98	−5.81	$4s^2$	$4p^6$
I^-	−17.42	−13.30	−16.32	$5s^2$	$5p^6$
K^+	−0.95		−0.91	$3s^2$	$3p^6$
Zn^{2+}	−7.36		−6.84	$3d^{10}$	
Sn^{2+}	−22.00		−20.65	$5s^2$	$5p^1$
Te^0	−18.40		−17.33	$5s^2$	$5p^4$
Fe^0	−8.99	−8.03	−8.26	$3d^6$	$4s^2$
Fe^+	−9.52	−8.49	−8.75	$3d^6$	$4s^1$
Fe^{2+}	−8.75	−7.80	−8.07	$3d^6$	
Fe^{3+}	−7.98	−7.13	−7.43	$3d^5$	

(Table II), do the two versions yield comparable results, because the approximations used in Eqs. (5) and (6) are less sensitive to contracted wavefunctions.

We make use of our results, obtained from the accurate CHF version, to compare them with literature values.

(1) It seems that the γ_∞ values for Be^0, B^+, Na^+, and K^+ derived from the analytic expansion CHF method[15-18] (AE-CHF) deviate from our values mainly because of the specific approach for the perturbed wave functions inherent to AE-CHF, which implies that the nodes being present in the unperturbed functions are rigidly preserved in the perturbed functions. Such a constraint may introduce significant inaccuracies in the calculations.[15]

(2) The LCMBP method is superior to the CHF and DEP methods in the sense that it includes correlation effects, while the CHF method neglects them partly and the DEP method neglects them completely. Correlation effects may account partly for the deviation of our γ_∞ results for Na^+ and Rb^+ from those obtained by the LCMBP and DEP method, respectively. Vajed-Samii *et al.*[7] and Ray *et al.*[19] derived from their LCMBP studies of Na^+ and Fe^{3+}, respectively, that correlation effects are of less importance than consistency effects. This is in qualitative agreement with our results in that, starting from $\gamma_\infty^1(\mathrm{Na}^+) = -4.64$ and $\gamma_\infty^1(\mathrm{Rb}^+) = -58.45$, we finally reached the convergent values $\gamma_\infty^{10}(\mathrm{Na}^+) = -7.09$ and $\gamma_\infty^{10}(\mathrm{Rb}^+) = -79.12$. Thus we conclude that the main deviation of our CHF results from LCMBP and DEP results is due to calculational differences which are not related with correlation effects.

(3) The considerable deviation of Ahmad's *et al.*[9] (LCMBPT) γ_∞ result for Pr^{3+} from our CHF result is probably due to their use of excited wavefunctions which were derived from the Hartree-Fock-Slater (HFS) program of Herman and Skillman.[20] From applications of the HFS program it is known[21,22] that for large distances from the nucleus the $X\alpha$ potential, which is used in this program, leads to an overestimation of the parametrized exchange integrals.[1] Recently, Sen and Weiss[23] have shown that the use of HFS functions for F^- and Cl^- leads to an increase in the magnitude of γ_∞ by about 100% compared to the use of HF functions.

IV. SUMMARY

The present study describes the application of Dalgarno's[6] CHF method of calculating Sternheimer functions $\gamma(r)$ for closed-shell systems. Deviating from the correct CHF procedure we have also introduced approximations in the calculation of exchange integrals to simplify the computational procedure. These approximations reduce the required computer time and memory space at least by a factor of 4 for each iteration, but lead to unreliable $\gamma(r)$ results unless the outermost valence electron shell has d^{10} configuration or is represented by relatively contracted wave functions. As far as MO calculations are concerned (which already include valence orbitals in their basis set) these approximations do not play an important role, because the Sternheimer corrections[1] R, γ_∞ (Table II) and $\gamma(r)$ are derived in this case from core wave functions only, which are contracted anyway.

We have compared our results obtained from the accurate CHF method with literature values derived from the AE-CHF, LCMBP, and DEP methods, respectively. Our conclusion is that consistency effects are considerably more important than correlation effects.

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APPENDIX

The angular coefficients C_i $(i=1,\ldots,9)$ in Eqs. (3) and (4) are defined as

$$C_1 = C_1(l_1, l, L) = \sum_m \langle Y_m^{l_1} | C_0^L | Y_m^{l_1} \rangle \langle Y_0^l | C_0^L | Y_0^l \rangle ,$$

$$C_2 = C_2(l_1, l, L) = \sum_m \langle Y_m^{l_1} | C_m^L | Y_0^l \rangle \langle Y_0^l | C_m^L | Y_m^{l_1} \rangle ,$$

$$C_3 = C_3(l_1, l', L) = \sum_m \langle Y_m^{l_1} | C_0^L | Y_m^{l_1} \rangle \langle Y_0^{l'} | C_0^L | Y_0^{l'} \rangle ,$$

$$C_4 = C_4(l_1, l', L) = \sum_m \langle Y_m^{l_1} | C_m^L | Y_0^{l'} \rangle \langle Y_0^{l'} | C_m^L | Y_m^{l_1} \rangle ,$$

$$C_5=C_5(l_1,l_1',l,l',L)=\sum_m \frac{\langle Y^{l_1'}_m|C^L_0|Y^{l_1}_m\rangle\langle Y^{l_1'}_m|C^2_0|Y^{l_1}_m\rangle\langle Y^{l'}_0|C^L_0|Y^{l}_0\rangle}{\langle Y^{l'}_0|C^2_0|Y^{l}_0\rangle},$$

$$C_6=C_6(l_1,l_1',l,l',L)=\sum_m \frac{\langle Y^{l_1}_m|C^L_m|Y^{l}_0\rangle\langle Y^{l_1'}_m|C^2_0|Y^{l_1}_m\rangle\langle Y^{l'}_0|C^L_m|Y^{l_1'}_m\rangle}{\langle Y^{l'}_0|C^2_0|Y^{l}_0\rangle},$$

$$C_7=C_7(l_1,l_1',l,l',L)=\sum_m \frac{\langle Y^{l_1'}_m|C^L_m|Y^{l}_0\rangle\langle Y^{l_1'}_m|C^2_0|Y^{l_1}_m\rangle\langle Y^{l'}_0|C^L_m|Y^{l_1}_m\rangle}{\langle Y^{l'}_0|C^2_0|Y^{l}_0\rangle},$$

$$C_8=C_8(l_1,l_1',l,l',L)=\sum_m \frac{\langle Y^{l_1'}_m|C^L_0|Y^{l_1}_m\rangle\langle Y^{l_1'}_m|C^2_0|Y^{l_1}_m\rangle\langle Y^{l}_0|C^L_0|Y^{l}_0\rangle}{\langle Y^{l'}_0|C^2_0|Y^{l}_0\rangle},$$

$$C_9=C_9(l_1,l_1',l,l',L)=\sum_m \frac{\langle Y^{l_1}_m|C^L_m|Y^{l}_0\rangle\langle Y^{l_1'}_m|C^2_0|Y^{l_1}_m\rangle\langle Y^{l_1'}_m|C^L_m|Y^{l}_0\rangle}{\langle Y^{l'}_0|C^2_0|Y^{l}_0\rangle}.$$

The symbols $Z_i(r)$ $(i=1,2,4,5,6,7)$ represent integral functions of the form

$$Z_i(r)=\int_0^r \frac{r'^L}{r^{L+1}}X_i(r')\mathcal{H}_i(r')dr' + \int_r^\infty \frac{r^L}{r'^{L+1}}X_i(r')\mathcal{H}_i(r')dr',$$

with

$$Z_1(r)=Z_1(n_1,l_1,L;r),\quad X_1=u^{(0)}_{n_1l_1},\quad \mathcal{H}_1=u^{(0)}_{n_1l_1},$$

$$Z_2(r)=Z_2(n,n_1,l,l_1,L;r),\quad X_2=u^{(0)}_{nl},\quad \mathcal{H}_2=u^{(0)}_{n_1l_1},$$

$$Z_4(r)=Z_4(n,n_1,l',l_1,L;r),\quad X_4=u^{(0)}_{n_1l_1},\quad \mathcal{H}_4=u^{(1)}_{nl'},$$

$$Z_5(r)=Z_5(n_1,l_1,l_1',L;r),\quad X_5=u^{(1)}_{n_1l_1'},\quad \mathcal{H}_5=u^{(0)}_{n_1l_1},$$

$$Z_6(r)=Z_6(n,n_1,l,l_1,L;r),\quad X_6=u^{(0)}_{n_1l_1},\quad \mathcal{H}_6=u^{(0)}_{nl}\quad [Z_2(r)\equiv Z_6(r)],$$

$$Z_7(r)=Z_7(n,n_1,l,l_1',L;r),\quad X_7=u^{(1)}_{n_1l_1'},\quad \mathcal{H}_7=u^{(0)}_{nl}.$$

Z_8 and Z_9 are double integrals given as

$$\begin{aligned}Z_8&=Z_8(n,n_1,l,l_1,l_1',L)\\&=\int_0^\infty |u^{(0)}_{nl}(r)|^2\left(\int_0^r \frac{r'^L}{r^{L+1}}u^{(1)}_{n_1l_1'}(r')u^{(0)}_{n_1l_1}(r')dr' + \int_r^\infty \frac{r^L}{r'^{L+1}}u^{(1)}_{n_1l_1'}(r')u^{(0)}_{n_1l_1}(r')dr'\right)dr,\end{aligned}$$

$$\begin{aligned}Z_9&=Z_9(n,n_1,l,l_1,l_1',L)\\&=\int_0^\infty u^{(1)}_{n_1l_1'}(r)u^{(0)}_{nl}(r)\\&\quad\times\left(\int_0^r \frac{r'^L}{r^{L+1}}u^{(0)}_{n_1l_1}(r')u^{(0)}_{nl}(r')dr' + \int_r^\infty \frac{r^L}{r'^{L+1}}u^{(0)}_{n_1l_1}(r')u^{(0)}_{nl}(r')dr'\right)dr.\end{aligned}$$

The coefficients C_i and Z_i are similar to those introduced by Sternheimer.[2]

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[1] S. Lauer, V. R. Marathe, and A. Trautwein, Phys. Rev. A 19, 1852 (1979).

[2] R. M. Sternheimer, Phys. Rev. 146, 140 (1966); extensive reference of Sternheimer's work on shielding is given in Ref. 1.

[3] A. Dalgarno, Proc. R. Soc. London A251, 282 (1959).

[4] S. Kaneko, J. Phys. Soc. Jpn. 11, 282 (1959).

[5] L. C. Allen, Phys. Rev. 118, 167 (1960).

[6] A. Dalgarno, Adv. Phys. 11, 281 (1962).

[7] M. Vajed-Samii, S. N. Ray, and T. P. Das, Phys. Rev. B 12, 4591 (1975).

[8] S. N. Ray, Taesul Lee, T. P. Das, and R. M. Sternheimer, Phys. Rev. A 9, 1108 (1974).

[9] S. Ahmad, and D. J. Newman, J. Phys. C11, L277 (1978).

[10] A. C. Beri, S. N. Ray, T. P. Das, and R. M. Sternheimer, Phys. Rev. A 12, 1168 (1975).

[11] S. Lauer, Diplomarbeit, Universität des Saarlandes, 1979 (unpublished).

[12] P. G. Khubchandani, R. R. Sharma, and T. P. Das, Phys. Rev. 126, 594 (1962).

[13] D. R. Hartree, *The Calculation of Atomic Structures* (Wiley, New York, 1957).

[14] In MO calculations the valence electron wave functions are used as a basis set of the MO's, and the remaining electron core which is perturbed by the nuclear quadruple moment Q is a closed-shell system.

[15] L. W. Langhoff, M. Karplus, and P. P. Hurst, J. Chem. Phys. 44, 505 (1966).

[16] J. Lahiri and A. Mukherji, Phys. Rev. 153, 386 (1967).

[17] J. Lahiri and A. Mukherji, Phys. Rev. 155, 24 (1967).

[18] P. K. Mukherjee, H. P. Roy, and A. Gupta, Phys. Rev. A 17, 30 (1978).

[19] S. N. Ray, Taesul Lee, and T. P. Das, Phys. Rev. A 9, 93 (1974).

[20] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Englewood Cliffs, New Jersey, 1963).

[21] J. E. Robinson, F. Bassoni, R. S. Knox, and J. R. Schrieffer, Phys. Rev. Lett. 9, 215 (1962).

[22] K. Schwarz, J. Phys. B11, 1339 (1978).
[23] K. D. Sen and A. Weiss, Theoret. Chim. Acta 52, 181 (1979).
[24] E. Clementi and C. Roetti, *Atomic and Nuclear Data Tables* (Pergamon, New York, 1974).
[25] E. Clementi, J. Chem. Phys. 38, 996 (1963); E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964).
[26] R. E. Watson and A. J. Freeman, Phys. Rev. 124, 1117 (1961).
[27] E. Clementi, IBM J. Res. Suppl. (1965).