Position moments linearly averaged over Hartree-Fock orbitals

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Linearly averaged position moments (LAPM's) are introduced for the Hartree-Fock orbitals. When all the LAPM's are well defined, the Hartree-Fock equation is shown to be equivalent to a set of relations between the LAPM's involving the potential-energy operator. The true Hartree-Fock orbitals must satisfy all the relations, and hence the LAPM equations can be used as a sensitive criterion to assess the accuracy of approximate Hartree-Fock orbitals. Such an application is presented for He, Be, and Ne atoms.

I. INTRODUCTION

In order to study the quality of wave functions, we have recently introduced[1,2] linearly averaged position moments (LAPM's), which are defined as the position moments averaged linearly (not quadratically) over the wave function. Based on the Schrödinger equation in a representation intermediate between the position and momentum ones, we have shown[1,2] that there exists a set of relationships among the LAPM's, the linearly averaged potential energy, and the total energy. These relations constitute a necessary condition for the true wave function, and they provide a sensitive criterion to assess the accuracy of approximate wave functions. The zero-momentum energy formula[3,4] or its modification[5] follows from the simplest case of the relations.

Very recently, it has also been shown[6] that the set of LAPM equations is equivalent to the original Schrödinger equation, provided all the LAPM's are well defined. The LAPM equation is a new form of the Schrödinger equation different from its differential form in position space and its integral form in momentum space. The deterministic property of the LAPM equation has been demonstrated[6] for the hydrogenlike atom, where the correct wave function and energy have been obtained from the solution of algebraic recurrence equations.

In the present paper, we report the LAPM equation corresponding to the Hartree-Fock equation for closed-shell systems. In the next section, the Hartree-Fock LAPM equation is derived in spherical polar coordinates and its properties are discussed, and its relationship with the zero-potential-energy expression[7,8] is also clarified. In Sec. III, application of the LAPM equation is illustrated for the assessment of the accuracy of approximate Hartree-Fock orbitals for He, Be, and Ne atoms. Atomic units are used throughout this paper.

II. FORMALISM

A. Hartree-Fock LAPM equation

The Hartree-Fock equation for a closed-shell $2N$ electron system with N doubly occupied spatial orbitals $\{\psi_i\}$ reads

$$\left[-\tfrac{1}{2}\Delta + v(\mathbf{r}) + \sum_{j=1}^{N} (2J_j - K_j) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) , \quad (1)$$

where the symbols have their usual meaning.[9] Multiplying both sides of Eq. (1) by $\exp(-i\mathbf{p}\cdot\mathbf{r})$ and integrating over the whole position space, we obtain an alternative form of the Hartree-Fock equation:

$$(p^2/2)[\exp(-i\mathbf{p}\cdot\mathbf{r})]_i + [\exp(-i\mathbf{p}\cdot\mathbf{r})v(\mathbf{r})]_i + \sum_{j=1}^{N} \{2[\exp(-i\mathbf{p}\cdot\mathbf{r})w_{jj}(\mathbf{r})]_i - [\exp(-i\mathbf{p}\cdot\mathbf{r})w_{ji}(\mathbf{r})]_j\} = \varepsilon_i [\exp(-i\mathbf{p}\cdot\mathbf{r})]_i ,$$

$$(2)$$

where

$$w_{ij}(\mathbf{r}) \equiv \int \frac{\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' , \quad (3)$$

$$[f(\mathbf{r})]_i \equiv \int f(\mathbf{r})\psi_i(\mathbf{r})d\mathbf{r} . \quad (4)$$

Note that the square brackets stand for the *linear* average over the orbital.

The plane-wave expansion of $\exp(-i\mathbf{p}\cdot\mathbf{r})$ is given by[10]

$$\exp(-i\mathbf{p}\cdot\mathbf{r})=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-i)^{l}j_{l}(pr)Y_{lm}(\Omega)Y_{lm}^{*}(\omega) ,$$

(5)

where (r,ω) and (p,Ω) are the spherical polar coordinates of the vectors $\mathbf{r}$ and $\mathbf{p}$, respectively. Y_{lm} is a spherical harmonic and j_{l} is the spherical Bessel function of the first kind which can be expanded as[11]

$$j_{l}(pr)=2^{l}\sum_{k=0}^{\infty}\frac{(-1)^{k}(k+l)!}{k!(2k+2l+1)!}(pr)^{2k+l} .$$

(6)

Substituting Eqs. (5) and (6) into Eq. (2), we can rearrange Eq. (2) as

$$\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}A_{kl}B_{i,klm}p^{2k+l}Y_{lm}(\Omega)=0 ,$$

(7)

where

$$A_{kl}=(-i)^{l}(-1)^{k}2^{l}(k+l)!/k!(2k+2l+1)! ,$$

(8)

$$B_{i,klm}=\delta_{i}^{(k,l,m)}[r^{2k+l}Y_{lm}^{*}(\omega)]_{i} ,$$

(9)

$$\delta_{i}^{(k,l,m)}=e_{i}^{(k,l,m)}-\varepsilon_{i} ,$$

(10)

in which $e_{i}^{(k,l,m)}$ is defined to be the LAPM orbital energy; it consists of the one-electron $e_{1,i}^{(k,l,m)}$ and two-electron $e_{2,i}^{(k,l,m)}$ parts:

$$e_{i}^{(k,l,m)}=e_{1,i}^{(k,l,m)}+e_{2,i}^{(k,l,m)} ,$$

(11)

$$e_{1,i}^{(k,l,m)}=\{-k(2k+2l+1)[r^{2k+l-2}Y_{lm}^{*}(\omega)]_{i}$$
$$+[r^{2k+l}v(\mathbf{r})Y_{lm}^{*}(\omega)]_{i}\}/[r^{2k+l}Y_{lm}^{*}(\omega)]_{i} ,$$

(12)

$$e_{2,i}^{(k,l,m)}=\sum_{j=1}^{N}\{2[r^{2k+l}w_{jj}(\mathbf{r})Y_{lm}^{*}(\omega)]_{i}$$
$$-[r^{2k+l}w_{ji}(\mathbf{r})Y_{lm}^{*}(\omega)]_{j}\}/[r^{2k+l}Y_{lm}^{*}(\omega)]_{i} .$$

(13)

In the one-electron part [Eq. (12)], only the orbital ψ_{i} under consideration appears, while in the two-electron part [Eq. (13)], all the occupied orbitals appear.

For Eq. (7) to be valid for any $\mathbf{p}=(p,\Omega)$, $B_{i,klm}$ must be zero, and hence at least one of the two factors on the right-hand side of Eq. (9) must vanish; thus

$$\delta_{i}^{(k,l,m)}=e_{i}^{(k,l,m)}-\varepsilon_{i}=0 ,$$

(14a)

or

$$[r^{2k+l}Y_{lm}^{*}(\omega)]_{i}=0 ,$$

(14b)

for *all* possible values of k, l, and m. When all the LAPM's appearing in Eqs. (12) and (13) are well defined, Eq. (14) is equivalent to the Hartree-Fock equation given by Eq. (1). Equation (14) is the Hartree-Fock LAPM equation, which may be used to determine the orbitals and the associated energies. It may be interesting to ob-

serve that the kinetic energy operator is implicit in Eq. (14). Note also that the w_{ij} appearing in Eqs. (12) are not moments in the usual sense. However, the solution of Eq. (14) does not seem to be straightforward, since the equation for the ith orbital includes all the occupied orbitals as is the case of the original equation (1). As a result, the LAPM equation (14) does not provide us any simpler procedure for the solution of the Hartree-Fock equation.

Alternatively we can use Eqs. (14) as criteria to assess the accuracy of Hartree-Fock orbitals: The true Hartree-Fock orbitals must satisfy Eqs. (14) for any k, l, and m, and Eqs. (14) constitute a necessary condition for the true Hartree-Fock orbitals. When we apply the criteria to atoms, Eqs. (14) are meaningful only for some specific l and m, since for other values of l and m, the original LAPM relation $B_{i,klm}=0$ is automatically satisfied due to the orthogonality of the spherical harmonics. On the other hand, there is no such restriction for the value of k so long as it is non-negative. Judging from the forms of the integrals involved in the LAPM expressions [Eqs. (12) and (13)], we expect that the relation with a larger k places more weight on the accuracy of the large-r region of a given orbital. This anticipation will be verified in the next subsection in connection with the zero-potential-energy criterion. Accuracy checks of some approximate Hartree-Fock orbitals based on Eq. (14a) are illustrated in Sec. III.

We note that a special and simplest case of Eq. (14a) for $k=l=m=0$ corresponds to the Hartree-Fock version of the zero-momentum (ZM) energy expression[3,4] and is given by

$$e_{i}^{(0,0,0)}=\varepsilon_{\mathrm{ZM},i}$$
$$=\left[[v(\mathbf{r})]_{i}+\sum_{j=1}^{N}\{2[w_{jj}(\mathbf{r})]_{i}-[w_{ji}(\mathbf{r})]_{j}\}\right]/[1]_{i} .$$

(15)

B. Relation to zero potential energy

For the particular case of $k\to\infty$, we can show that the *atomic* LAPM orbital energy $e_{i}^{(k,l,m)}$ coincides with the zero potential (ZP) orbital energy[7,8] $\varepsilon_{\mathrm{ZP},i}$.

To do this, we first recognize the following relation. For a large r, let two exponentially decaying functions $F(r)$ and $G(r)$ satisfy an inequality $F(r)>G(r)$. Then we have

$$\lim_{n\to\infty}\left[\int_{0}^{\infty}r^{n}G(r)dr\bigg/\int_{0}^{\infty}r^{n}F(r)dr\right]=0 ,$$

(16)

where the two integrals are assumed to exist for all n.

For an atom with nuclear charge Z, the LAPM's appearing in Eqs. (11)–(13) explicitly take the following forms:

$$[r^{2k+l}Y_{lm}^{*}]_{i}=\int_{0}^{\infty}r^{2k+l+2}f_{i}(r)dr ,$$

(17a)

$$[r^{2k+l-2}Y_{lm}^{*}]_{i}=\int_{0}^{\infty}r^{2k+l}f_{i}(r)dr ,$$

(17b)

$$[r^{2k+l}vY_{lm}^{*}]_{i}=\int_{0}^{\infty}r^{2k+l+2}g_{i}(r)dr ,$$

(17c)

TABLE I. Accuracy of Hartree-Fock $1s$ orbital assessed by the LAPM equation for the He atom.

Basis set	ε_{1s}	k	$e_{1s}^{(k,0,0)}$	$\delta_{1s}^{(k,0,0)}$
Single-ζ	$-0.896\,48$	0	$-1.000\,00$	$-0.103\,52$
		1	$-1.145\,94$	$-0.249\,46$
		2	$-1.231\,63$	$-0.355\,15$
		3	$-1.278\,93$	$-0.382\,45$
		4	$-1.307\,82$	$-0.411\,34$
		5	$-1.327\,15$	$-0.430\,67$
Double-ζ	$-0.917\,94$	0	$-0.922\,18$	$-0.004\,24$
		1	$-0.937\,48$	$-0.019\,54$
		2	$-0.958\,50$	$-0.040\,56$
		3	$-0.977\,18$	$-0.059\,24$
		4	$-0.991\,37$	$-0.073\,43$
		5	$-1.001\,77$	$-0.083\,83$
Near-Hartree-Fock	$-0.917\,95$	0	$-0.918\,66$	$-0.000\,71$
		1	$-0.922\,33$	$-0.004\,38$
		2	$-0.929\,86$	$-0.011\,91$
		3	$-0.939\,27$	$-0.021\,32$
		4	$-0.948\,35$	$-0.030\,40$
		5	$-0.956\,09$	$-0.038\,14$

$$[r^{2k+l}w_{jj}Y_{lm}^{*}]_i = \int_0^{\infty} r^{2k+l+2}h_{jj,i}(r)dr \ , \qquad (17\text{d})$$

$$[r^{2k+l}w_{ji}Y_{lm}^{*}]_j = \int_0^{\infty} r^{2k+l+2}h_{ji,j}(r)dr \ , \qquad (17\text{e})$$

where

$$f_i(r) = \int Y_{lm}^{*}(\omega)\psi_i(r,\omega)d\omega \ , \qquad (18\text{a})$$

$$g_i(r) = \int Y_{lm}^{*}(\omega)v(r,\omega)\psi_i(r,\omega)d\omega = -(Z/r)f_i(r) \ , \qquad (18\text{b})$$

TABLE II. Accuracy of Hartree-Fock orbitals assessed by the LAPM equation for the Be atom.

Orbital	Basis set	ε_i	k	$e_i^{(k,0,0)}$	$\delta_i^{(k,0,0)}$
$1s$	Single-ζ	$-4.717\,12$	0	$-4.320\,98$	$+0.396\,13$
			1	$-1.328\,28$	$+3.388\,84$
			2	$-0.416\,91$	$+4.300\,21$
			3	$-0.376\,33$	$+4.340\,79$
	Double-ζ	$-4.732\,83$	0	$-4.653\,37$	$+0.079\,46$
			1	$-1.766\,53$	$+2.966\,30$
			2	$-0.199\,91$	$+4.532\,92$
			3	$-0.168\,60$	$+4.564\,23$
	Near-Hartree-Fock	$-4.732\,67$	0	$-4.727\,80$	$+0.004\,87$
			1	$-4.232\,20$	$+0.500\,47$
			2	$-0.789\,87$	$+3.942\,80$
			3	$-0.218\,63$	$+4.514\,04$
$2s$	Single-ζ	$-0.308\,64$	0	$-0.314\,63$	$-0.005\,99$
			1	$-0.333\,13$	$-0.024\,49$
			2	$-0.355\,14$	$-0.046\,50$
			3	$-0.372\,95$	$-0.064\,31$
	Double-ζ	$-0.309\,23$	0	$-0.306\,83$	$+0.002\,40$
			1	$-0.291\,20$	$+0.018\,03$
			2	$-0.254\,97$	$+0.054\,26$
			3	$-0.217\,77$	$+0.091\,46$
	Near-Hartree-Fock	$-0.309\,27$	0	$-0.309\,31$	$-0.000\,04$
			1	$-0.309\,34$	$-0.000\,07$
			2	$-0.308\,91$	$+0.000\,36$
			3	$-0.307\,39$	$+0.001\,88$

$$h_{ij,k}(r)=\int Y_{lm}^{*}(\omega)\left[\int \frac{\psi_i^{*}(\mathbf{r}')\psi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right]\psi_k(r,\omega)d\omega .$$

(18c)

For a large r, the leading asymptotic behavior of an atomic Hartree-Fock orbital is known[12,13] to be

$$f_i(r)=[a_i r^{b_i}+O(r^{b_i-1})]\exp(-\zeta_i r) ,$$

(19)

in which a_i is an unknown proportionality constant, and the exponent ζ_i is determined by orbital energies. In particular, $\zeta_i=(-2\varepsilon_i)^{1/2}$ for those few atoms like H, He, Li, and Be in which only s orbitals are occupied, and $\zeta_i=(-2\varepsilon_h)^{1/2}$ in which h labels the highest occupied orbital for all other atoms. Based on Eq. (19), we can show after some manipulation that

$$h_{jj,i}(r)=(1/r)f_i(r) ,$$

(20a)

$$h_{ji,j}(r)=\begin{cases}O(e^{-r})f_i(r) & \text{for } s\text{-type atom}\\ (1/r^{\lambda})f_i(r) & \text{otherwise ,}\end{cases}$$

(20b)

for a large r, where $O(e^{-r})$ represents an exponential decay, and where λ is a positive integer. Then, from Eqs. (12), (13), and (16), we have

$$\lim_{k\to\infty}e_{1,i}^{(k,l,m)}=\lim_{k\to\infty}\frac{-k(2k+2l+1)\int_0^{\infty}r^{2k+l}f_i(r)dr}{\int_0^{\infty}r^{2k+l+2}f_i(r)dr} ,$$

(21a)

$$\lim_{k\to\infty}e_{2,i}^{(k,l,m)}=0 .$$

(21b)

For a very large value of k, the integrals appearing in Eq.

TABLE III. Accuracy of Hartree-Fock orbitals assessed by the LAPM equation for the Ne atom. The index l is 0 for the s orbitals and is 1 for the $2p$ orbital.

Orbital	Basis set	ε_i	k	$e_i^{(k,l,0)}$	$\delta_i^{(k,l,0)}$
$1s$	Single-ζ	-32.66213	0	-30.93028	$+1.73185$
			1	-14.47640	$+18.18573$
			2	-4.86014	$+27.80199$
			3	-3.70685	$+28.95528$
	Double-ζ	-32.75988	0	-32.46044	$+0.29944$
			1	-22.54428	$+10.21560$
			2	-7.22100	$+25.53888$
			3	-4.59613	$+28.16375$
	Near-Hartree-Fock	-32.77248	0	-32.73354	$+0.03894$
			1	-29.82847	$+2.94401$
			2	-16.51263	$+16.25985$
			3	-12.76598	$+20.00650$
$2s$	Single-ζ	-1.73250	0	-1.88553	-0.15303
			1	-2.21140	-0.47890
			2	-2.56226	-0.82976
			3	-2.83720	-1.10470
	Double-ζ	-1.92187	0	-1.91201	$+0.00986$
			1	-1.88402	$+0.03785$
			2	-1.86403	$+0.05784$
			3	-1.87809	$+0.04378$
	Near-Hartree-Fock	-1.93043	0	-1.92719	$+0.00324$
			1	-1.91038	$+0.02005$
			2	-1.88157	$+0.04886$
			3	-1.87317	$+0.05726$
$2p$	Single-ζ	-0.56172	0	-1.37401	-0.81229
			1	-2.04253	-1.48081
			2	-2.50682	-1.94510
			3	-2.81521	-2.25349
	Double-ζ	-0.84143	0	-0.97586	-0.13443
			1	-1.17093	-0.32950
			2	-1.35246	-0.51103
			3	-1.48947	-0.64804
	Near-Hartree-Fock	-0.85044	0	-0.84055	$+0.00989$
			1	-0.82189	$+0.02855$
			2	-0.81330	$+0.03714$
			3	-0.82271	$+0.02773$

(21a) are expected to be governed by the large-r asymptotic behavior of the function $f_i(r)$. Inserting the asymptotic expression (19) in Eqs. (21) leads to

$$\lim_{k \to \infty} e_{1,i}^{(k,l,m)} = -(\zeta_i^2/2) \ , \tag{22a}$$

and hence

$$\lim_{k \to \infty} e_i^{(k,l,m)} = \varepsilon_{ZP,i} \ , \tag{22b}$$

where $\varepsilon_{ZP,i}$ is the zero potential orbital energy defined[8] by

$$\varepsilon_{ZP,i} \equiv \lim_{r \to \infty} [-\tfrac{1}{2}\Delta\psi_i(\mathbf{r})]/\psi_i(\mathbf{r})$$

$$= -(\zeta_i^2/2) \ . \tag{23}$$

Equation (22b) is the desired result. Clearly, when a LAPM relation [Eq. (14a)] with a large value of k is employed as a criterion of accuracy, more importance will be attached to the tail quality of the orbital.

III. APPLICATIONS: ACCURACY OF HARTREE-FOCK ORBITALS ASSESSED BY LAPM EQUATION

We have applied the LAPM equations (14) to the assessment of the accuracy of Hartree-Fock orbitals for the He, Be, and Ne atoms. The single-ζ, double-ζ, and near-Hartree-Fock wave functions reported by Clementi and Roetti[14] have been examined.

In Table I, the results for the He $1s$ orbital are summarized, where only results for the nontrivial case $l = m = 0$ are shown with the index k varying from 0 to 5. When one goes from the single-ζ to the near-Hartree-Fock wave function, the accuracy of the orbital measured by the smallness of $|\delta_{1s}^{(k,0,0)}|$ increases. However, the LAPM measure is found to be very sensitive to the error. In the case of the near-Hartree-Fock calculation, for example, the calculated orbital energy differs from the true value[15] $-0.917\,96$ only by 1×10^{-5}, but the LAPM energy assigns the error 7.1×10^{-4} even for $k = 0$. This is due to the linear dependence of the LAPM energy on the orbital error. Another remarkable trend found in Table I is that in all the three cases, the accuracy decreases as the index k increases. As has been discussed in the preceding section, this is a reflection of poor description of the large-r tail region of the orbital compared to the small- and intermediate-r regions, and suggests that it is rather difficult to determine the correct asymptotic behavior of Hartree-Fock orbitals using the simple basis-set expansion scheme.

Table II shows the results for the Be atom, where the indices l and m are again zero. As in the case of the He atom, the LAPM criterion reveals that (i) the best accura-

cy is found for the near-Hartree-Fock wave function and (ii) the accuracy decreases as k increases. However, quite different qualities of the core $1s$ and valence $2s$ orbitals are observed in this table. In the case of the near-Hartree-Fock wave function, the calculated orbital energies agree with the exact values[15] completely. Accordingly, the LAPM error is rather small for the $2s$ orbital. However, this is not true for the inner $1s$ orbital; the error for $k = 0$ may be acceptable, but for $k = 3$ the relative error amounts to 95%. As Eqs. (11)–(13) imply, the LAPM energy does not directly reflect the quality of the orbital under examination, since all the occupied orbitals participate through the two-electron part. A finer analysis shows, however, that the major contribution comes from the one-electron part especially when k increases. Therefore, the larger error for the $1s$ orbital may be interpreted as an indication of the poor tail quality of this orbital, which is ineffective energetically. In this sense, we can say that the Be $2s$ orbital of the near-Hartree-Fock wave function is the most accurate orbital among the six orbitals examined in this study.

The results for the three occupied orbitals of the Ne atom are presented in Table III. The index m is 0 for all orbitals, but l is 0 and 1 for the s and p orbitals, respectively. The two remarks given for the He and Be atoms are also valid for the Ne atom. Moreover, we may draw the same conclusion, as in the case of Be, about the different quality of the $1s$ and $2s$ orbitals. Though the $2p$ orbital is a new type of orbital, it does not seem to have any special tendency; an exception is that even when $k = 0$ the LAPM measure assigns a poor quality for the single-ζ approximation relative to the other orbitals. When we examine the relative LAPM error (defined by $|\delta_i^{(k,l,0)}/\varepsilon_i|$), we find that the $2s$ orbital is more accurate than the $2p$ orbital for all the three approximate wave functions. In these wave functions, the number of s-type basis functions is about twice the number of p-type ones. We anticipate that among orbitals of the same symmetry, a Hartree-Fock calculation in the basis-function-expansion scheme tends to give more asymptotic freedom to the outer orbitals ($2s$ orbital in this case) at the expense of the large-r quality of the inner orbitals ($1s$ orbital in this case), as a consequence of the energy-minimization requirement.

IV. SUMMARY

We have derived the Hartree-Fock LAPM equation and discussed its properties. The equation has been applied to the assessment of the accuracy of approximate Hartree-Fock orbitals. The high sensitivity of the LAPM criterion has been demonstrated and the different quality of the inner and outer orbitals resulting from Roothaan-Hartree-Fock calculations has been clarified.

[1]T. Koga, J. Chem. Phys. **89**, 5961 (1988).

[2]T. Koga, J. Chem. Phys. **90**, 5887 (1989).

[3]B. H. Armstrong, Bull. Am. Phys. Soc. **9**, 401 (1964); Lockheed Missiles and Space Company Technical Report, Physics No. 6-74-64-26, 1964 (unpublished).

[4]A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **18**, 841 (1978).

[5]T. Koga, K. Ohta, and A. J. Thakkar, Phys. Rev. A **37**, 1411

(1988).

[6]T. Koga, J. Chem. Phys. **91**, 4774 (1989).

[7]T. Koga, J. Chem. Phys. **83**, 6301 (1985).

[8]T. Koga, J. Chem. Phys. **89**, 4209 (1988).

[9]C. C. J. Roothan, Rev. Mod. Phys. **23**, 69 (1951).

[10]A. Messiah, *Quantum Mechanics*, (North-Holland, Amsterdam, 1981), Vol. 1, p. 497.

[11]*Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972), p.

435.

[12]N. C. Handy, M. T. Marron, and H. J. Silverstone, Phys. Rev. **180**, 45 (1969).

[13]G. S. Handler, D. W. Smith, and H. J. Silverstone, J. Chem. Phys. **73**, 3936 (1980).

[14]E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[15]C. Froese Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977), pp. 28–30.