$\langle 1/r^3 \rangle$ and $Q(0)$ as they would be for Hartree-Fock wave functions.

[15] R. W. B. Ardill and A. L. Stewart, J. Chem. Phys. 47, 4853 (1967); Proc. Phys. Soc. (London) 92, 296 (1967).

[16] D. A. Goodings, Phys. Rev. 123, 1706 (1961).

[17] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) 73, 811 (1959).

[18] G. D. Gaspari, W. M. Shyu, and T. P. Das, Phys. Rev. 134, A852 (1964).

[19] W. Marshall, J. Phys. Soc. Japan 17, Suppl. B-120 (1962).

[20] Burke (Ref. 12b) has also concluded that the concept of core polarization by non-s electrons is valid, but Bergreen and Wood [Phys. Rev. 130, 198 (1963)] question the idea of core polarization by s electrons.

[21] J. B. Martin and A. W. Weiss, J. Chem. Phys. 39, 1618 (1963).

[22] T. Koopmans, Physica 1, 104 (1933).

[23] Here the orbitals are taken to be real, $\langle 1a | 1b \rangle$ denotes an overlap integral, $\langle 1a | h | 1b \rangle$ denotes a one-electron integral, and

$$(\alpha\beta | \gamma\delta) = \int d\vec{x}_1 \phi_\alpha{}^*(1)\phi_\beta(1) \times \int d\vec{x}_2 (1/r_{12}) \phi_\gamma{}^*(2) \phi_\delta(r)$$

is the usual notation for a two-electron integral. We have multiplied (4) by $(1+\frac{1}{2}\langle 1a | 1b \rangle^2)$ for convenience.

[24] Comparing the $\rho(0)$ for the HF wave function of Li^+ to the value for the very accurate Pekeris wave function [Phys. Rev. 126, 143 (1962)], $\rho(0)=13.704$, we would expect the $\rho(0)$ for the various states of Li in Table II to also be lower than the exact values by about 0.03 or 0.2%.

[25] R. Isler, S. Marcus, and R. Novick, Bull. Am. Phys. Soc. 11, 62 (1966).

[26] B. Budick, H. Bucka, R. J. Goshen, A. Landman, and R. Novick, Phys. Rev. 147, 1 (1966).

[27] For example, see R. E. Trees, Phys. Rev. 92, 308 (1953).

[28] E. R. Cohen and J. W. M. Dumond, Rev. Mod. Phys. 37, 537 (1965).

[29] N. F. Ramsey, Molecular Beams (Oxford, Clarendon Press, London, 1956) p. 172.

[30] The basic idea of using a configuration interaction approach to prove this theorem was suggested by Professor R. M. Pitzer, private communication, 1966.

[31] J. F. Perkins, J. Chem. Phys. 42, 3927 (1965).

[32] E. Hylleraas and B. Undheim, Z. Physik 65, 759 (1930); J. K. L. MacDonald, Phys. Rev. 43, 830 (1933).

[33] W. A. Goddard, III, J. Chem. Phys. 48, 5337 (1968).

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Relativistic Calculations of Electron Binding Energies by a Modified Hartree-Fock-Slater Method

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Relativistic atomic wave functions and electron binding energies have been calculated by a modified Hartree-Fock-Slater method. The local exchange approximation, originally introduced by Slater, is modified in such a way that the total energy of the system is minimized. Approximate expressions for the optimum exchange potential are suggested for all atoms and ions. The total atomic energies and electron binding energies obtained by this method agree extremely well with the corresponding Hartree-Fock results in the cases where such data are available. Various corrections to the theoretical binding energies are discussed, in particular the effect of rearrangement during the ionization process. It is found that this effect is of importance for inner shells in all elements and is responsible for the main discrepancy between experimental and previous theoretical results for light and medium-heavy elements. For heavy elements other effects are of importance, and various possible sources of the residual discrepancy between theory and experiments are discussed.

I. INTRODUCTION

During the last decade our knowledge of electron binding energies in atoms has increased considerably, due in particular to the development of the electron-spectroscopic method (ESCA) by Siegbahn *et al.*[1] This method has been applied to almost all elements between lithium and berkelium and to inner as well as outer shells. The accuracy of the new data is so high that improved theoretical calculations are justified. The electron binding energies are often used to check the accuracy of electronic wave functions. When the accuracy of the calculations increases, several effects have to be taken into account. Besides the relativistic effects, which of course are dominant for heavy elements, it is necessary to consider relaxation mechanisms, correlation effects, core polarization, quantum-electrodynamic effects, and nuclear-size effects. These effects are discussed in this paper.

With present data techniques the Hartree-Fock (HF) equations, at least in the so-called "restricted" scheme, can be treated for all atoms. The corresponding relativistic equations can also in principle be solved, but so far only a few such calculations have been presented.[2-5] It has been previously[6] shown, however, and is demonstrated further in this paper that accurate electron binding energies can be obtained without use of the comparatively complicated HF scheme. A simpler procedure is also needed in other applications. The exchange potential obtained in the HF methods is nonlocal, that is, it depends not only on the space coordinates but also on the value of the electron wave function. In band-structure calculations, e.g., by the augmented plane wave method, only local potentials can be handled, and good atomic approximations are required as a starting point. During the last few years considerable interest has been devoted to the problem of finding the "best" local approximation to the HF potential in free atoms and ions. The first local exchange potential was suggested by Slater.[7] His approximation, now usually referred to as the Hartree-Fock-Slater (HFS) method, has been extensively used, e.g., in the atomic calculations by Herman and Skillman[8] and by Liberman *et al.*[9] and in numerous band-structure calculations.[10] By a slightly different derivation, Gáspár[11] obtained an exchange potential, which is $\frac{2}{3}$ of Slater's potential. This approximation has recently been discussed by Kohn and Sham[12] and Cowan *et al.*[13] Neither of these two approximations, however, represents the best local approximation of the HF potential. One of us (I. L.) has shown[6] that, by introducing two adjustable parameters in Slater's expression, an appreciable improvement could be achieved in the nonrelativistic case as judged by the total energy. The "optimized" potential was found to yield total energies, as well as electron binding energies, remarkably close to the HF values. Once the parameters have been determined, this method can be employed as easily as any other method of the Slater type. In the present paper these calculations are extended to the relativistic case and comparisons are made with HF results, where such data are available.

II. METHOD OF CALCULATION

A. General

The Dirac equation for an electron in a spherically symmetric potential $V(r)$ is

$$H\phi=[c\vec{\alpha}\cdot\vec{p}+\beta m_0c^2+V(r)]\,\phi=E\phi, \tag{1}$$

where $\vec{p}$ is the momentum operator, c the velocity of light, m_0 the rest mass of the electron, and $\vec{\alpha}$ and β are the Dirac matrices

$$\vec{\alpha}=\begin{pmatrix}0 & \vec{\sigma}\\ \vec{\sigma} & 0\end{pmatrix},\quad \beta=\begin{pmatrix}I & 0\\ 0 & -I\end{pmatrix}\ . \tag{2}$$

$\vec{\sigma}$ represents here the Pauli spin matrices and I is a 2×2 unit matrix. The wave function ϕ is a four-component function of the form

$$\phi=\begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix}\quad , \tag{3}$$

where ϕ_1 and ϕ_2 are two-component functions of the Pauli type.

By subtracting the rest energy of the electron, Eq. (1) becomes

$$H'\phi=[c\vec{\alpha}\cdot\vec{p}+(\beta-1)m_0c^2+V(r)]\phi=e\phi\ . \tag{4}$$

The Dirac Hamiltonian in Eq. (4) commutes with the total electron angular momentum $\vec{j}$ and with the parity operator $P=\beta P_0$, where P_0 is the conventional parity operator.[14] We can then find simultaneous eigenfunctions $\phi_{\omega jm}$ of H, $\vec{j}^2$, j_z, and P with the eigenvalues $j(j+1)$, m, and $(-1)^{j+\omega/2}$, respectively, where $\omega=\pm1$. In this way ϕ_1 has the parity $j+\omega/2$, and ϕ_2 has the parity $j-\omega/2$. The $\phi_{\omega jm}$ are also eigenfunctions of the operator K with eigenvalues $-\omega(j+\frac{1}{2})=-\kappa$, and of K^2 with eigenvalues $(j+\frac{1}{2})^2=\kappa^2$. Here K is given by

$$K=\beta(\vec{\sigma}'\cdot\vec{L}+1), \tag{5}$$

$$\text{where}\quad \vec{\sigma}'=\begin{pmatrix}\vec{\sigma} & 0\\ 0 & \vec{\sigma}\end{pmatrix}. \tag{6}$$

κ can take the values $\pm(j+\frac{1}{2})$; the values of ω and j are uniquely determined by the value of κ.

The spin-angular dependence of the functions ϕ_1 and ϕ_2 is given by

$$\mathcal{Y}_{ljm}(\theta,\varphi,\sigma)=\sum_{\sigma=\pm\frac{1}{2}}\langle l\,\tfrac{1}{2}\,m-\sigma\,\sigma\,|\,l\tfrac{1}{2}jm\rangle\times Y_{l,\,m-\sigma}(\theta,\varphi)\,\chi(\sigma), \tag{7}$$

obtained by vector coupling of the normalized spherical harmonics $Y_{l,\,\mu}(\theta,\varphi)$ and the spinors by

$$\chi(\tfrac{1}{2})=\begin{pmatrix}1\\0\end{pmatrix},\quad \chi(-\tfrac{1}{2})=\begin{pmatrix}0\\1\end{pmatrix}. \tag{8}$$

The functions $\phi_{\omega jm}$ can then be written

$$\phi_{\omega jm}=\begin{pmatrix}[F(r)/r]\,\mathcal{Y}_{ljm}(\theta,\varphi,\sigma)\\ \\ [i\,G(r)/r]\,\mathcal{Y}_{\bar{l}jm}(\theta,\varphi,\sigma)\end{pmatrix}\ , \tag{9}$$

where $l=j+\omega/2$ and $\bar{l}=j-\omega/2$. By inserting this wave function into Eq. (4), one gets the two coupled differential equations for the radial functions

$$\frac{dF}{dr} = -\frac{\kappa}{r} F + \frac{1}{c}\left[e - V(r) + 2m_0c^2\right] G ,$$
$$\frac{dG}{dr} = \frac{\kappa}{r} G - \frac{1}{c}\left[e - V(r)\right] F, \tag{10}$$

where the quantum number κ is given by

$$\kappa = j + \tfrac{1}{2} \quad \text{for } l = j + \tfrac{1}{2} ,$$
$$\kappa = -\left(j + \tfrac{1}{2}\right) \quad \text{for } l = j - \tfrac{1}{2} . \tag{11}$$

For many-electron atoms the Hamiltonian is in the first approximation (in Hartree atomic units[15])

$$H = \sum_i \left[c\vec{\alpha}_i \cdot \vec{p}_i + (\beta_i - 1)c^2 - \frac{Z}{r_i}\right] + \sum_{i<j} \frac{1}{r_{ij}} . \tag{12}$$

Here magnetic interactions and retardation effects (Breit interactions) are neglected. These can later be treated as perturbations. The wave function is assumed to be an antisymmetrized product of orthonormal spin-orbitals ϕ_i (Slater determinant). The total energy then becomes

$$E = \sum_i \langle i|f|i\rangle + \sum_{i<j} \langle ij|g|ij\rangle , \tag{13}$$

where

$$\langle i|f|i\rangle = \int \phi_i(1)^* \left[c\vec{\alpha} \cdot \vec{p} + (\beta - 1)c^2 - Z/r\right] \phi_i(1) d\tau_1$$

and

$$\langle ij|g|ij\rangle = \iint \phi_i(1)^* \phi_j(2)^* \frac{1 - P_{12}}{r_{12}} \times \phi_i(1)\phi_j(2) d\tau_1 d\tau_2 .$$

Here P_{12} is the exchange operator and r_{12} is the inter-electron distance. As in the nonrelativistic case, application of the variational principle leads to the (nonlocal) HF potential

$$V_i(\vec{r}_1) = -\frac{Z}{r_1} + \sum_j \int \phi_j(2)^* \frac{1 - P_{12}}{r_{12}} \phi_j(2) d\tau_2 . \tag{14}$$

In the approximation introduced by Slater,[7] the HFS procedure, the potential is assumed to be spherically symmetric and the exchange part is replaced by a local term

$$V_{ex}(r_1) = -\left[81\rho(r_1)/32\pi^2 r_1^2\right]^{1/3} , \tag{15}$$

where $\rho(r_1)$ is the radial electron density

$$\rho(r_1) = \sum_j \left[F_j(r_1)^2 + G_j(r_1)^2\right] . \tag{16}$$

In this approximation the total potential is the same for *all* electrons and becomes

$$V(r_1) = -\frac{Z}{r_1} + \frac{1}{r_1} \int_0^{r_1} \rho(r_2) dr_2 + \int_{r_1}^{\infty} \frac{\rho(r_2)}{r_2} dr_2 + V_{ex}(r_1) . \tag{17}$$

At large values of r this potential does not approach the correct Coulomb potential. Therefore, the potential [Eq. (17)] is normally replaced by this limiting potential at points where the Coulomb potential is larger (Latter's correction[16]).

In the nonrelativistic treatment the HFS wave function has been considerably improved[6] by the introduction of a parametrized exchange potential of the form

$$V_{ex}'(r_1) = -(C/r_1)\left[81 r_1^n \rho(r_1)^m / 32\pi^2\right]^{\frac{1}{3}} , \tag{18}$$

where C, n, and m are adjustable parameters (equal to unity in HFS approximation). The parameters are determined by minimizing the total energy of the system. The total energies and the electron binding energies obtained in this way are remarkably close to those obtained by the HF method.[6] It has been found that for practical purposes it is sufficient to vary only the parameters C and n. The optimum value of m is very close to unity. Furthermore, the parameters need not be determined separately for each element, degree of ionization, configuration, etc., but the same parameter combination can be used over large regions of the periodic table.

Gáspár,[11] Kohn and Sham,[12] and Cowan *et al.*[13] have suggested an exchange potential, which is two-thirds of the Slater's potential (i.e., $C = \frac{2}{3}$, $n = m = 1$). This modification represents a significant improvement over the original Slater method (as measured by the total energy), but does not yield the same good agreement with the HF results as does the optimized potential above. For free atoms or ions the optimized potential is, in principle, the best local potential that approximates the nonlocal HF potential and is therefore a good starting point for calculations on more complicated systems, e.g., for band-structure calculations on solids.

From Eqs. (4) and (13) one obtains for the eigenvalue of electron i

$$e_i = \langle i|H'|i\rangle = \langle i|f|i\rangle + \langle i|V_i(r) + Z/r|i\rangle . \tag{19}$$

In the HF scheme one gets from Eqs. (13) and (14)

$$\sum_j \langle ij|g|ij\rangle - \langle i|V_i(\vec{r}) + Z/r|i\rangle = 0, \tag{20}$$

which together with Eqs. (13) and (19) gives

$$E = \sum_i e_i - \tfrac{1}{2} \sum_i \langle i|V_i(r) + Z/r|i\rangle . \tag{21}$$

In other methods, such as HFS, Eq. (20) is not exactly valid due to the approximations in the potential and has to be replaced by

$$\sum_j \langle ij|g|ij\rangle - \langle i|V(r)+Z/r|i\rangle = \delta\epsilon_i \,. \tag{22}$$

This gives the total energy

$$E = \sum_i e_i - \tfrac{1}{2}\sum_i \langle i|V(r)+Z/r|i\rangle + \tfrac{1}{2}\sum_i \delta\epsilon_i \,. \tag{23}$$

The expressions above are identical to the corresponding nonrelativistic ones, if e_i represents the eigenvalue of the corresponding nonrelativistic Hamiltonian.[6] The last term in Eq. (23) is a correction which has been neglected in most earlier applications of the HFS method.[8,9] The correction is, however, considerably larger than the difference in total energy between different approximations considered here and has to be included to make a comparison between the methods meaningful (see Table II).

The expression (23) for the total energy involves a summation of electrostatic integrals over all electron pairs. The summation of the direct and exchange integrals over one closed shell can be written

$$\sum_{m_b}\left\langle ab\left|\frac{1}{r_{12}}\right|cb\right\rangle = \sum_{m_b}\left[\left(ab\left|\frac{1}{r_{12}}\right|cb\right) - \left(ab\left|\frac{1}{r_{12}}\right|bc\right)\right]$$

$$= \delta(l_a, l_c)\delta(j_a, j_c)(2j_b+1) \times\left[R^0(abcb) - \sum_k R^k(abbc)\begin{pmatrix} j_a & k & j_b \\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}^2\right], \tag{24}$$

where $R^0(abcb)$ and $R^k(abbc)$ are radial integrals given by

$$R^k(abcd) = \iint [F_a(r_1)F_c(r_1) + G_a(r_1)G_c(r_1)] \times [F_b(r_2)F_d(r_2) + G_b(r_2)G_d(r_2)]\,\frac{r_<^k}{r_>^{k+1}}\,dr_1 dr_2 \,.$$

This agrees with the expression given by Grant,[17] although some of his coefficients are in error.[5]
In the case of unclosed shells the average energy for the configuration is calculated according to the method described by Slater.[7]

TABLE I. Parameters [as defined in Eq. (18)] of the optimized potential. (In all cases $m = 1$.)

Z	Atom		C	n
		Nonrelativistic		
9	F	$2p^5$	0.94	1.36
11	Na	$2p^63s$	0.82	1.17
11	Na$^+$	$2p^6$	0.92	1.28
13	Al	$3p$	0.84	1.20
16	S	$3p^4$	0.82	1.15
18	A	$3p^6$	0.82	1.17
19	K	$3p^64s$	0.72	1.01
19	K$^+$	$3p^6$	0.84	1.20
21	Sc	$3d4s^2$	0.77	1.10
24	Cr	$3d^44s^2$	0.78	1.12
26	Fe	$3d^64s^2$	0.79	1.15
29	Cu	$3d^{10}4s$	0.85	1.24
29	Cu$^+$	$3d^{10}$	0.88	1.30
		Relativistic		
29	Cu	$3d^{10}4s$	0.85	1.25
36	Kr	$4p^6$	0.77	1.12
53	I	$5p^5$	0.75	1.10
63	Eu	$4f^76s^2$	0.75	1.10
80	Hg	$5d^{10}6s^2$	0.75	1.12
84	Po	$6p^4$	0.72	1.08
92	U	$5f^36d$	0.70	1.06
		General		
$10 \lesssim$	$Z \lesssim 40$		0.80	1.15
$40 \lesssim$	Z		0.75	1.10

The parameters in Eq. (18) have been determined for a number of atoms by minimizing the total relativistic energy calculated according to Eq. (23). The optimum values are collected in Table I together with the nonrelativistic values for light elements. For copper an optimization has been performed relativistically as well as nonrelativistically, and the results agree within the numerical uncertainties. One can therefore with good reason assume that the parameters determined nonrelativistically can be used in relativistic calculations and *vice versa*.

When the optimum parameter values are plotted in a diagram (see Fig. 1), they fall in a narrow band in the C-n plane, i.e., there is a strong correlation between the two parameters. One also finds that there is a tendency of the optimum values to move along this band from the upper right to the

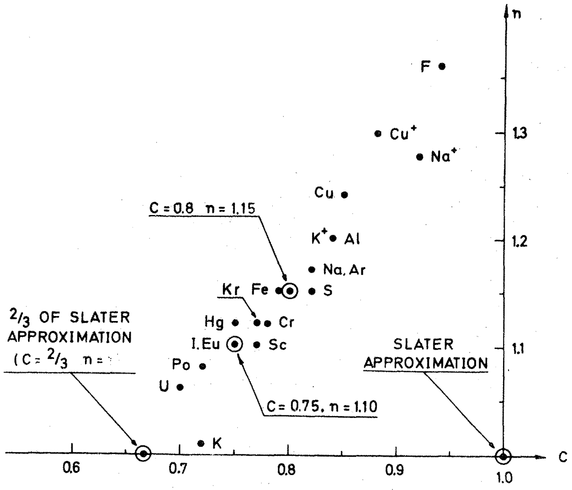

FIG. 1. Parameters [as defined in Eq. (18)] of the optimized exchange potential. (In all cases $m = 1.0$.)

lower left of the diagram as Z increases. For very heavy elements the optimum exchange potential becomes relatively close to the approximation suggested by Gáspár and others[11-13] ($C = \frac{2}{3}$, $n = 1$), while for lighter elements it differs appreciably from that approximation. The energy surface is such that the slope along the band in the C-n plane, where most optimum points fall, is very much smaller than the slope perpendicular to that band. Therefore the absolute values of the two parameters are not very critical, as long as one chooses a combination at the bottom of the energy valley. This means that it is possible to find "general" parameter combinations, which can be used for a large number of elements. These are given at the bottom of Table I. For very light elements ($Z < 10$) a statistical approach is less justified and no systematic investigation has been performed.

We have also made an optimization for some ions and found that the results are close to those obtained for the corresponding atom with the same electron configuration (see Table I and Fig. 1). As a rule, when ionized and excited states are considered, the general parameters given in Table I represent good approximations.

Recently Berrondo and Goscinski[18] have suggested a further modification of the local exchange approximation in the nonrelativistic case. They pointed out that in approximations of the Slater type, the virial theorem is not usually fulfilled. By the introduction of a "scaling parameter" it is possible, without any further computations, to obtain a solution with a lower total energy, for which the virial theorem is satisfied. The optimum scaling factor is

$$\eta = 1 + \delta = -V/2T,$$

where V is the potential and T is the kinetic energy before scaling. The total energy E is then reduced by the amount $|\delta^2 E|$. Berrondo and Goscinski[18] have shown that when the scaling procedure is applied to the Slater approximation, the difference in the total energy between the HFS and HF approximations is reduced by approximately a factor of 2. By optimizing the potential according to Eq. (18), we have obtained a corresponding reduction by a factor of 5–6. It should be observed that Berrondo and Goscinski in contrast to us do not normally use the Latter correction (see above), which makes comparison between the results difficult. When the Latter correction is omitted, the total energy seems to be somewhat reduced in most cases. Potentials obtained in such a way, however, have little relevance for excited states, since the asymptotic behavior is not correct. We have therefore preferred to keep the Latter correction in all cases. When the exchange potential is optimized according to our procedure, the virial theorem is very nearly fulfilled ($\delta < 0.001$), in the nonrelativistic calculations and hence no significant improvement can be achieved by scaling. In the relativistic case the virial theorem has another form[4] and so far has not been applied in our calculations.

B. Calculations of Binding Energies

The binding energy of an electron in a free atom or ion is defined as the work required to remove the electron from its orbit to infinity with no kinetic energy. This ionization process leaves the system in an excited state, and the binding energy is essentially equal to the difference in the total energy immediately after and before the ionization. In the first approximation the removal of an electron does not change the field inside the atom, and one may assume that the orbitals of the other electrons remain unchanged during the process ("frozen orbitals"). The binding energy of an electron k is then [from Eq. (13)]

$$\begin{aligned} B_k &= E(\text{ion}) - E(\text{atom}) \\ &= -\langle k|f|k\rangle - \sum_j \langle kj|g|kj\rangle \ . \end{aligned} \tag{25}$$

In the general HF scheme this is according to Eqs. (19) and (20) (apart from sign) equal to the one-electron eigenvalue for electron k (Koopmans' theorem).[19] In other approximations, e.g., of HFS type, Koopmans's theorem is not exactly valid, and one has to correct the one-electron eigenvalue e_k to get the binding energy B_k.[6] In a similar way to the total energy above, one obtains

$$B_k = -e_k - \delta e_k \ , \tag{26}$$

where δe_k is the correction defined in Eq. (22). This correction, which is usually not considered in HFS calculations,[8,9] has been found to be comparatively large, of the order of 100 eV for the 1s electron in medium-heavy and heavy elements. As illustrated in Table III, the agreement with the HF values is much improved when this correction is included. This method of calculating the binding energy is here referred to as "method A."

For more accurate calculations of electron binding energies, the effect of the ionization on the remaining electron orbitals has to be taken into account. Two cases can be distinguished. If the relaxation time is short compared with the time for the ionization process, one can assume that the excited state has reached its equilibrium before the electron is removed. In this case the total energy of the excited (ionic) state is best obtained by a separate self-consistent-field (SCF) procedure. The binding energy is given by the difference between the total energy of the excited state and that of the ground state. This method is here referred to as "method B." If the relaxation time is comparatively long, the electron orbitals can be assumed to be unchanged during the ionization process. In this case the total energy of the excited state is best obtained using the "frozen" orbitals of the atomic ground state. This means that the binding energy is obtained in a single SCF calculation (method A).

The two methods of calculating the binding energy are illustrated in a simple way in Fig. 2. There the energy is schematically drawn as a function of a single-parameter wave function. The energy minimum represents the "true" wave function. When atomic orbitals are used for the excited state (method A), the minimum is not ob-

TABLE II. Total relativistic atomic energies (Hartree units). Numbers in parentheses are Hartree-Fock values.

		Conventional HFS		Modified HFS		
Z	Atom	uncorrected	corrected	$c=\frac{2}{3}$ $n=m=1$	General parameters	Optimized potential
8	O $2p^4$	73.9607	74.7775	74.7747	74.8001	
9	F $2p^5$	98.5176	99.4469	99.4467	99.4787	99.4871
10	Ne $2p^6$	127.591	128.624	128.631	128.662	(128.692)[4]
11	Na $3s$	160.774	162.000	162.056	162.065	162.065
12	Mg $3s^2$	198.487	199.853	199.912	199.921	(199.935)[3]
13	Al $3p$	240.714	242.243	242.302	242.313	242.314
14	Si $3p^2$	287.681	289.354	289.416	289.430	
15	P $3p^3$	339.554	341.386	341.452	341.467	
16	S $3p^4$	396.499	398.485	398.555	398.574	398.574
17	Cl $3p^5$	458.681	460.820	460.896	460.914	
18	Ar $3p^6$	526.264	528.553	528.637	528.658	528.658
19	K $4s$	598.930	601.385	601.501	601.503	601.505
20	Ca $4s^2$	676.975	679.565	679.684	679.686	
21	Sc $3d4s^2$	760.494	763.221	763.343	763.351	763.352
22	Ti $3d^24s^2$	849.789	852.656	852.784	852.795	
23	V $3d^34s^2$	945.013	948.025	948.162	948.174	
24	Cr $3d^54s$	1046.296	1049.418		1049.576	
24	Cr $3d^44s^2$	1046.322	1049.483	1049.627		1049.641
25	Mn $3d^54s^2$	1153.864	1157.146	1157.300	1157.315	
26	Fe $3d^64s^2$	1267.792	1271.195	1271.360	1271.376	1271.376
27	Co $3d^74s^2$	1388.260	1391.786	1391.959	1391.977	
28	Ni $3d^84s^2$	1515.420	1519.071	1519.253	1519.273	
29	Cu $3d^{10}4s$	1649.470	1653.192	1653.197	1653.403	1653.406
30	Zn $4s^2$	1790.433	1794.344		1794.568	
31	Ga $4p$	1938.151	1942.290	1942.507	1942.523	
32	Ge $4p^2$	2092.850	2097.184	2097.407	2097.423	
33	As $4p^3$	2254.620	2259.156	2259.385	2259.402	
34	Se $4p^4$	2423.540	2428.301		2428.555	
35	Br $4p^5$	2599.810	2604.731	2604.975	2604.991	
36	Kr $4p^6$	2783.46	2788.556	2788.807	2788.825	2788.826
37	Rb $5s$	2974.204	2979.493	2979.775	2979.775	
38	Sr $5s^2$	3172.298	3177.767	3178.054	3178.053	
49	In $5p$	5872.88	5880.09	5880.48	5880.49	
51	Sb $5p^3$	6472.66	6480.21	6480.61	6480.61	
52	Te $5p^4$	6785.70	6793.41	6793.81	6793.82	
53	I $5p^5$	7107.65	7115.51	7115.92	7115.93	7115.93
54	Xe $5p^6$	7438.60	7446.62	7447.04	7447.05	
55	Cs $6s$	7778.35	7786.51		7786.96	
56	Ba $6s^2$	8127.14	8135.42			
59	Pr $4f^36s^2$	9229.54	9238.03		9238.52	
63	Eu $4f^76s^2$	10 837.88	10 846.71	10847.23	10 847.25	10 847.25
66	Dy $4f^{10}6s^2$	12 152.96	12 161.90		12 162.48	
67	Ho $4f^{11}6s^2$	12 612.85	12 621.84		12 622.42	
68	Er $4f^{12}6s^2$	13 083.76	13 092.80			
69	Tm $4f^{13}6s^2$	13 565.85	13 574.95			
74	W $5d^46s^2$	16 147.93	16 157.82	16 158.47	16 158.49	
77	Ir $5d^76s^2$	17 839.01	17 849.29		17 850.00	
78	Pt $5d^96s$	18 427.32	18 437.75	18 438.43	18 438.46	
79	Au $5d^{10}6s$	19 028.26	19 038.81	19 039.51	19 039.53	
80	Hg $5d^{10}6s^2$	19 641.95	19 652.59	19 653.31	19 653.33	19 653.33 (19 653.7)[3]
81	Tl $6p$	20 268.31	20 279.08	20 279.82	20 279.83	
83	Bi $6p^3$	21 560.17	21 571.17	21 571.93	21 571.94	
84	Po $6p^4$	22 226.08	22 237.14	22 237.91	22 237.92	22 237.92
86	Rn $6p^6$	23 598.83	23 609.98	23 610.78	23 610.79	
92	U $5f^36d$	28 057.71	28 068.81	28 069.70	28 069.70	28 069.71
95	Am $5f^7$	30 494.34	30 505.11	30 506.04	30 506.05	

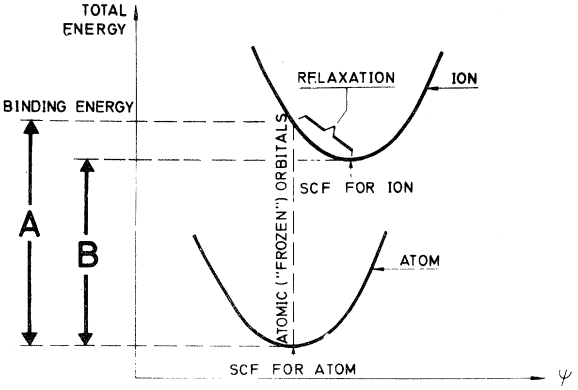

FIG. 2. Comparison of methods A and B for calculating electron binding energies.

tained, but could be reached if the orbitals are allowed to relax (method B). This means that method A always gives a larger binding energy than method B, which has been verified in all numerical examples. Method A is also sensitive to small changes in the wave function, which is not the case for method B provided that the correct expression for the energy [Eq. (23)] is used. This is illustrated below for some typical cases (see Table IX).

III. RESULTS AND COMPARISON WITH EXPERIMENTS

In nonrelativistic applications of the modified HFS method described above amazingly good agreement with HF binding energies has been obtained.[6] It would therefore be of great interest to test this method also in the relativistic case. When these calculations started the only relativistic HF calculation for a heavy element available to us was the calculations by Mayers on mercury, quoted by Liberman *et al.*[2] We therefore selected mercury as our first example. The results of these calculations are presented in Table III. Column 3 gives the uncorrected eigenvalues with the original Slater potential (in principle, identical to the values given by Liberman *et al.*[9]) and column 4 the corresponding values corrected for the nonvalidity of Koopmans's theorem[19] according to Eq. (25). The next two columns give the corrected binding energies obtained with the potential suggested by Gáspár and others[11–13] and our optimized potential, respectively. The results of two HF calculations, some binding energies obtained by method B (see previous section) and finally the experimental results are presented in the remaining columns.

The binding energies calculated by use of the modified HFS method with optimized exchange potential are found to be almost identical with the HF results. This is quite remarkable in view of the approximations involved. As a matter of fact our results agree even better with the recent HF values of Coulthard[3] than do the earlier HF values of Mayers.[2]

The experimental values in Table III are taken from the table of Bearden[20] and corrected for the work function, except for the outermost electrons, where optical data[21] are used (marked with †).

In Tables IV–VIII we show in a similar way the results for Cu, Kr, I, Eu, and U, for which the optimum exchange potential has been determined. Besides that we have calculated the binding energies for a large number of atoms by use of the "general" parameters given in Table I, but these data are too extensive to be given here.

Figure 3 shows the difference between the theoretical binding energy of the 1*s* electron calculated according to methods A and B, respectively, and the corresponding experimental results. From the results in Tables III–VIII and Fig. 3 one finds that for inner shells method B (separate orbitals for atom and ion) gives binding energies in much better agreement with the experimental results than does method A ("frozen" orbitals for the ion). This is particularly the case for light and medium-heavy elements. The result can be interpreted by assuming that the relaxation time is very short, that is, the orbitals find their new equilibrium in a time which is short compared with the time for the ionization process. For the outermost electrons, on the other hand, method A seems to yield better results. This indicates that the relaxation time is comparatively long for these orbitals, which is quite understandable from an elementary point of view.

As discussed above (see Fig. 2) the choice of approximation is not critical when the electron binding energy is calculated according to method B. This fact is further demonstrated in Table IX, where some typical results obtained by different methods are compared. The difference between the various HFS and HF results is found to be quite negligible (probably within the numerical uncertainty), provided that the total energy is calculated in the correct way according to Eq. (23). If the energy is not corrected for the effects due to the nonvalidity of Koopmans's theorem,[19] but calculated according to the approximate relation [Eq. (21)], quite different results are obtained with the various HFS potentials and the agreement with the HF results is in general not particularly good.

As shown above there exists a significant residual discrepancy between the theoretical and experimental binding energies, particularly for inner shells in heavy atoms. Possible sources of error are the following:

(a) numerical uncertainties,
(b) exchange effects,
(c) correlation effects,
(d) polarization effects,
(e) relaxation effects,
(f) nuclear-size effects,
(g) chemical and solid-state effects,
(h) magnetic and retardation effects, and
(i) quantum-electrodynamic effects.

The calculations described here are carried out to a high degree of numerical accuracy and the numerical uncertainty in the binding energies is normally less than a few electron volts. For inner shells errors of this order of magnitude are negligible.

TABLE III. Electron binding energies for mercury (Hartree units). Experimental values marked with † are taken from the optical data of Ref. 21; all other experimental values are from Ref. 20.

			Binding energy, method A						
Shell	*j*	Eigenvalue Slater potential	Slater potential	2/3 of Slater potential	Optimized potential	Hartree-Fock (Coulthard)	Hartree-Fock (Mayers)	Binding energy method B	Experimental
1*s*	1/2	3065.10	3072.93	3076.26	3076.15	3076.15	3076.18	3072.70	3054.19
2*s*	1/2	545.16	548.02	550.68	550.50	550.54	550.56	548.41	545.51
2*p*	1/2	523.88	524.22	527.01	526.85	526.86	526.88	524.55	522.34
	3/2	451.52	452.61	455.30	455.13	455.14	455.17	453.04	451.60
3*s*	1/2	130.07	131.40	133.34	133.14	133.18	133.20	131.90	131.06
3*p*	1/2	120.34	120.82	122.81	122.61	122.64	122.66	121.32	120.65
	3/2	104.25	104.80	106.71	106.52	106.54	106.58		104.80
3*d*	3/2	88.01	87.59	89.60	89.41	89.43	89.96	88.15	87.81
	5/2	84.54	84.20	86.19	86.00	86.02	86.04		84.50
4*s*	1/2	28.97	29.64	30.82	30.66	30.67	30.76	30.04	29.58
4*p*	1/2	24.75	25.10	26.28	26.12	26.13	26.13	25.50	25.04
	3/2	20.84	21.23	22.34	22.19	22.19	22.22		21.15
4*d*	3/2	13.90	13.84	14.95	14.80	14.80	14.80	14.27	14.07
	5/2	13.17	13.12	14.21	14.05	14.05	14.06		13.39
4*f*	5/2	4.167	3.573	4.627	4.476	4.469	4.472	3.999	3.93
	7/2	4.004	3.424	4.465	4.315	4.308	4.294		3.79
5*s*	1/2	4.628	4.687	5.225	5.125	5.106	5.108	4.896	4.59
5*p*	1/2	3.213	3.147	3.648	3.553	3.538	3.538	3.344	3.12
	3/2	2.511	2.497	2.942	2.856	2.842	2.846	2.687	2.28
5*d*	3/2	0.587	0.402	0.723	0.659	0.650	0.646	0.543	0.614†
	5/2	0.512	0.344	0.644	0.584	0.575	0.576	0.483	0.545†
6*s*	1/2	0.352	0.257	0.359	0.340	0.328	0.328	0.312	0.384†
Total energy		19641.95	19652.59	19653.31	19653.33	19653.7			

In calculations of the Slater type the exchange effect is treated approximately, introducing some errors. In the modified version used here these errors are negligibly small, provided that corrections for the nonvalidity of Koopmans's theorem are applied. The presented results can therefore be regarded as practically identical to relativistic Hartree-Fock results based on the Hamiltonian [Eq. (12)].

The main approximation in the Hartree-Fock scheme is that the electrons are assumed to move independently of each other, i.e., correlation effects are neglected. When the correlation is included, the total energy of the system is reduced. Since the correlation effect increases with the number of electrons, it is larger in the neutral atom than in ionized states of the same atom. Therefore the binding energy is expected to increase when the correlation is considered. As seen from the Tables III-VIII, the theoretical

TABLE IV. Electron binding energies for copper (Hartree units). (See also Table III caption.)

			Binding energy, method A				
Shell	*j*	Eigenvalue Slater potential	Slater potential	$\frac{2}{3}$ of Slater potential	Optimized potential	Binding energy method B	Experimental
1*s*	1/2	328.67	331.36	331.38	332.58	330.81	330.14
2*s*	1/2	39.92	40.77	40.78	41.56	40.69	40.48
2*p*	1/2	35.23	35.38	35.38	36.22	35.27	35.11
	3/2	34.45	34.62	34.62	35.46	34.52	34.38
3*s*	1/2	4.458	4.777	4.777	5.134	4.851	4.57
3*p*	1/2	2.960	3.062	3.062	3.411	3.143	2.87
	3/2	2.861	2.966	2.967	3.310	3.048	
3*d*	3/2	0.371	0.188	0.188	0.470	0.274	0.39†
	5/2	0.360	0.178	0.178	0.457	0.265	
4*s*	1/2	0.261	0.219	0.219	0.252	0.242	0.284†
Total energy		1649.47	1653.19	1653.20	1653.41		

TABLE V. Electron binding energies for krypton (Hartree-units). (See also Table III caption.)

Shell	*j*	Eigenvalue Slater potential	Binding energy, method A			Binding energy method B	Experimental
			Slater potential	$\frac{2}{3}$ of Slater potential	Optimized potential		
1*s*	1/2	524.80	528.19	529.86	529.65	527.68	526.47
2*s*	1/2	69.92	71.02	72.22	72.01	71.05	70.60
2*p*	1/2	63.52	63.76	65.02	64.82	63.75	63.47
	3/2	61.50	61.78	63.03	62.82	61.77	61.55
3*s*	1/2	10.23	10.71	11.34	11.20	10.88	(10.6)
3*p*	1/2	7.908	8.106	8.738	8.602	8.272	8.18
	3/2	7.605	7.809	8.429	8.295	7.974	7.86
3*d*	3/2	3.504	3.265	3.897	3.762	3.428	3.27
	5/2	3.452	3.218	3.845	3.711	3.380	
4*s*	1/2	1.009	1.062	1.248	1.197	1.136	1.012†
4*p*	1/2	0.494	0.437	0.584	0.546	0.498	0.539†
	3/2	0.467	0.414	0.552	0.517	0.474	0.514†
Total energy		2783.45	2788.56	2788.81	2788.83		

binding energies are in almost all cases too large, and the agreement with experiment is not generally improved by taking correlation effects into account. Furthermore, the effects are definitely too small to be of importance for inner shells in heavy elements. For outer shells, on the other hand, the effects are more important.

Most Hartree-Fock calculations, as well as the HFS calculations presented here, are "restricted" in the sense that all electrons in one shell (same n, l, and j) are assumed to have the same radial distribution. For atoms with closed shells only, like mercury, this treatment is exact in the Hartree-Fock sense. However, when an inner electron is removed, the symmetry is drastically disturbed, and the electron shells become polarized. This reduces the energy of the ionic state and, therefore, changes the binding energy in the right direction. The effect of the polarization is now being investigated quantitatively.

The binding energy for an atomic electron is determined as the difference in total energy after and before the ionization process. The energy after the ionization is determined here in two ways, either by use of "frozen" atomic orbitals (method A) or by use of self-consistent orbitals for the ion (method B). Both methods are, of course, very crude and can only be considered as reliable in the two limiting cases, long and short relaxation times, respectively. In the intermediate cases

TABLE VI. Electron binding energies for iodine (Hartree units). (See also Table III caption).

Shell	*j*	Eigenvalue Slater potential	Binding energy, method A			Binding energy method B	Experimental
			Slater potential	$\frac{2}{3}$ of Slater potential	Optimized potential		
1*s*	1/2	1218.89	1224.02	1226.21	1226.02	1223.56	1219.13
2*s*	1/2	189.72	191.51	193.13	192.95	191.67	190.81
2*p*	1/2	178.52	178.97	180.70	180.51	179.08	178.46
	3/2	167.37	167.98	169.67	169.49	168.11	167.62
3*s*	1/2	38.79	39.60	40.60	40.45	39.91	39.55
3*p*	1/2	34.08	34.40	35.42	35.27	34.71	34.34
	3/2	31.96	32.29	33.29	33.14		32.29
3*d*	3/2	23.57	23.21	24.28	24.12	23.52	23.35
	5/2	23.12	22.78	23.84	23.68		22.91
4*s*	1/2	7.020	7.308	7.827	7.729	7.525	7.00
4*p*	1/2	5.347	5.431	5.937	5.841	5.645	4.66
	3/2	4.928	5.025	5.513	5.420		
4*d*	3/2	2.202	1.959	2.406	2.320	2.150	1.97
	5/2	2.135	1.895	2.337	2.251		
5*s*	1/2	0.770	0.759	0.920	0.883	0.835	0.766†
5*p*	1/2	0.394	0.334	0.456	0.430	0.395	
	3/2	0.352	0.305	0.412	0.390	0.362	0.412†
Total energy		7107.65	7115.51	7115.92	7115.93		

TABLE VII. Electron binding energies for europium (Hartree units). Experimental values are from Refs. 20 and 25.

			Binding energy, method A				
Shell	j	Eigenvalue Slater potential	Slater potential	$\frac{2}{3}$ of Slater potential	Optimized potential	Binding energy method B	Experimental
1s	1/2	1785.17	1791.33	1793.97	1793.76	1790.95	1783.23
2s	1/2	294.70	296.90	298.95	298.72	297.12	296.06
2p	1/2	280.21	280.72	282.88	282.65	280.88	280.08
	3/2	256.08	256.88	258.99	258.76	257.11	256.55
3s	1/2	65.30	66.29	67.72	67.51	66.60	66.30
3p	1/2	58.94	59.35	60.81	60.60	59.67	59.46
	3/2	53.99	54.36	55.79	55.58		54.56
3d	3/2	42.88	42.53	44.02	43.81	42.88	42.80
	5/2	41.79	41.37	42.86	42.65		41.71
4s	1/2	13.14	13.55	14.39	14.24	13.79	13.61[25]
4p	1/2	10.66	10.90	11.72	11.57	11.15	10.77[25]
	3/2	9.558	9.690	10.48	10.34		9.73[25]
4d	3/2	5.423	5.378	6.122	5.986	5.636	5.34[25]
	5/2	5.224	4.875	5.629	5.490		5.13[25]
4f	5/2	0.351	0.013	0.566	0.465	0.238	0.415[25]
	7/2	0.325	-0.088	0.460	0.361		
5s	1/2	1.808	1.807	2.106	2.039	1.923	1.32
5p	1/2	1.124	1.028	1.289	1.231	1.128	
	3/2	0.975	0.861	1.098	1.044		0.88
6s	1/2	0.190	0.151	0.190	0.182	0.174	
Total energy		10837.88	10846.71	10847.23	10847.25		

the ionization process has to be examined in greater detail. As mentioned above, the agreement with experiments is much improved for inner shells in light and medium-heavy elements, when the ion is allowed to relax during the ionization process (method B). For heavier elements this is not the case. For the 1s level in mercury, for instance, the difference between theory and experiment is 598 eV in method A and 504 eV in method B. Therefore it is obvious that the major part of the discrepancy must be due to other causes.

The effect of the finite nucleus on the wave functions and binding energies has been investigated. The results for mercury are given in Table X for surface and uniform charge distributions, with a nuclear radius given by $R = 1.2A^{1/3} \times 10^{-13}$ cm where A is the mass-number of the isotope considered. It is seen that the effect on the eigenvalues is significant but quite small. When the correction for the nonvalidity of Koopmans's theorem is applied, the effect of the finite nucleus is much reduced. The reason for this is not clear. However, it is evident that the effect on the binding energy is negligible in the cases considered here compared with other effects. The eigenvalues for a uniform charge distribution are within the limits of error in agreement with those obtained by Bhalla.[22]

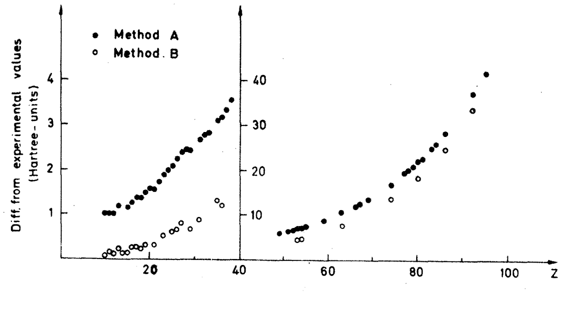

FIG. 3. The difference between the theoretical binding energy of the 1s electron calculated according to methods A and B, respectively, and the corresponding experimental values.

Most experimental determinations of electron binding energies are made on solids, while the theoretical investigations described here are concerned with free atoms. Experimentally, "chemical" effects, i.e., variation in the binding energy between different chemical compounds, of the order of 5–10 eV have been observed.[1] One can expect the difference between the binding energies in the solid and in the free atom to be of the same order of magnitude. The experimental values for outer electrons given in Tables III-VI are taken from optical data, and hence no solid-state correction is required. For inner shells the effect is comparatively small, although not quite negligible. A more detailed calculation of this effect, e.g., by the tight binding method,[23] could possibly improve further the agreement between theory and experiment for light elements.

The Hamiltonian (12) used in the present calculations is only approximate, since magnetic inter-

TABLE VIII. Electron binding energies for uranium (Hartree units). Experimental values are from Ref. 20.

			Binding energy, method A				
Shell	*j*	Eigenvalue Slater potential	Slater potential	$\frac{2}{3}$ of Slater potential	Optimized potential	Binding energy method B	Experimental
1s	1/2	4273.41	4282.33	4286.02	4286.06	4282.24	4248.69
2*s*	1/2	801.10	804.40	807.33	807.32	804.98	799.74
2*p*	1/2	773.45	773.39	776.48	776.47		769.98
	3/2	631.37	632.63	635.57	635.55		631.01
3*s*	1/2	203.18	204.79	206.94	206.89		204.04
3*p*	1/2	190.45	190.97	193.18	193.14		190.59
	3/2	157.61	158.28	160.37	160.32		158.30
3*d*	3/2	137.30	136.87	139.08	139.04		137.14
	5/2	130.61	130.29	132.47	132.42		130.67
4*s*	1/2	52.24	53.10	54.46	54.40		53.10
4*p*	1/2	46.46	46.90	48.26	48.21		46.92
	3/2	37.85	38.33	39.59	39.54		38.55
4*d*	3/2	28.58	28.52	29.80	29.74		28.83
	5/2	26.99	26.94	28.19	28.14		27.26
4*f*	5/2	14.75	14.01	15.29	15.23		14.53
	7/2	14.33	13.59	14.85	14.79		14.15
5*s*	1/2	11.79	11.94	12.67	12.62		12.04
5*p*	1/2	9.520	9.496	10.20	10.16		9.68
	3/2	7.457	7.483	8.124	8.081		7.32
5*d*	3/2	4.112	3.885	4.459	4.420		4.01
	5/2	3.802	3.476	4.046	4.005		3.69
5*f*	5/2	0.313	0.044	0.395	0.369		
6*s*	1/2	1.914	1.877	2.189	2.161		2.75
6*p*	1/2	1.245	1.143	1.417	1.392		1.70
	3/2	0.895	0.778	1.009	0.987		1.33
6*d*	3/2	0.170	0.118	0.212	0.206		0.26
7*s*	1/2	0.211	0.158	0.218	0.212		
Total energy		28 057.71	28 068.81	28 069.70	28 069.71		

actions and retardation effects (Breit interactions) are neglected. Smith and Johnson[5] have calculated these effects to be about – 0.05 eV for the 1*s* level in argon, while Grant[17] has obtained a value of the order of – 200 eV for the unretarded magnetic contribution to the binding energy of the 1s electron in mercury. More detailed calculations of the effects of the various Breit interactions are desired and are now being prepared by use of our modified HFS functions.

As far as we can see, there is only one remaining effect which can be of importance for the binding energy of inner electrons, namely quantum-electrodynamic effects (Lamb shift). If Grant's value for the effect of the Breit interactions is used, there is a residual discrepancy for the 1*s* electron in mercury of about 300 eV. By using hydrogen wave functions Brown and Mayers[24] have estimated the effect of the Lamb shift to be of the order of – 500 eV for the 1*s* binding energy in mercury. This is of the right order of magnitude

TABLE IX. Comparison between electron binding energies calculated according to method B (see text) in various approximations. The uncorrected and corrected values are calculated by use of Eqs. (21) and (23), respectively (Hartree units).

Approximation	Ne 2*s*	Mg 2*s*	Hg 1*s*
Slater potential uncorrected	1.60	3.26	3072.2
Optimum potential uncorrected	1.48	3.10	3061.0
Slater potential corrected	1.81	3.59	3072.7
Optimum potential corrected	1.80	3.59	3072.7
Hartree-Fock (Ref. 3)	1.81	3.58	3072.5

TABLE X. Comparison of eigenvalues and electron binding energies for mercury calculated with the Slater potential and different nuclear charge distributions (method A) (Hartree units).

	Difference from point charge values in Table III			
	Uniform charge distribution		Surface charge distribution	
Shell	Eigenvalue	Binding energy	Eigenvalue	Binding energy
1*s*	1.91	0.28	2.89	0.45
2*s*	0.29	0.039	0.43	0.064
3*s*	0.065	0.009	0.099	0.014
4*s*	0.017	0.002	0.025	0.003
5*s*	0.003	• • •	0.005	• • •

to explain the residual discrepancy. A more careful calculation of these effects would be highly desirable.

The calculations described here have been performed on the CDC 3600 computer at the University of Uppsala and on the IBM 360/50 computer at Chalmers University of Technology, Göteborg.

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[1] K. Siegbahn *et al.*, in ESCA, Atomic, Molecular and Solid-State Structure Studied by Means of Electron Spectroscopy (Almqvist-Wiksells Bokh. AB, Uppsala, 1967).

[2] D. F. Mayers, quoted by Liberman *et al.*, Phys. Rev. 137, A27 (1965).

[3] M. A. Coulthard, Proc. Phys. Soc. (London) 91, 44 (1967).

[4] Young-Ki Kim, Phys. Rev. 154, 17 (1967).

[5] F. C. Smith and W. R. Johnson, Phys. Rev. 160, 136 (1967).

[6] I. Lindgren, Phys. Letters 19, 382 (1965); Arkiv Fysik 31, 59 (1966).

[7] J. C Slater, Phys. Rev. 81, 385 (1951); and Quantum Theory of Atomic Structure (McGraw Hill Book Co., Inc., New York, 1960).

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

[9] D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. 137, A27 (1965); E. C. Snow, J. Canfield, and J. T. Waber, Phys. Rev. 135, A969 (1964).

[10] T. L. Loucks, Augmented-plane-wave method (W. A. Benjamin, Inc., New York, 1967).

[11] R. Gáspár, Acta Phys. Acad. Sci. Hung. 3, 263 (1954).

[12] W. Kohn and L. S. Sham, Phys. Rev. 140, A1133 (1965); B. Y. Tong and L. S. Sham, Phys. Rev. 144, 1 (1966).

[13] R. D. Cowan *et al.*, Phys. Rev. 144, 5 (1966).

[14] M. E. Rose, Relativistic Electron Theory (John Wiley & Sons, Inc., New York, 1961).

[15] In this system c has the value $1/\alpha$, where α is the fine-structure constant. We have here kept c in the equations in order to avoid confusion with the Dirac operator $\vec{\alpha}$.

[16] R. Latter, Phys. Rev. 99, 510 (1955).

[17] I. P. Grant, Proc. Roy. Soc. (London) A262, 555 (1961).

[18] M. Berrondo and O. Goscinski, Quantum Chemistry group, University of Uppsala Report No. 198, 1967 (unpublished).

[19] T. Koopmans, Physica 1, 104 (1933).

[20] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. 39, 125 (1967).

[21] C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

[22] C. P. Bhalla, Phys. Rev. 157, 1136 (1967).

[23] J. R. Reitz, Solid State Physics, edited by F. Zeitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1.

[24] G. E. Brown and D. F. Mayers, Proc. Roy. Soc. (London) A251, 105 (1959).

[25] Ö. Nilsson, C.-H. Norberg, J.-E. Bergmark, A. Fahlman, C. Nordling, and K. Siegbahn, to be published.