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Optimized effective atomic central potential*

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A self-consistent set of equations is derived for an atomic central potential such that the energy given by the orbitals for the potential is minimized. It is shown that this effective potential behaves like $-e^2/r$ for large r values. The equations have been solved for carbon, neon, and aluminum, and the resulting total energies exceed the Hartree-Fock total energies by less than 0.005%. The theory leads to an effective, local, central exchange potential analogous to the $X\alpha$ potential.

I. INTRODUCTION

It has long been known[1,2] that the Slater determinant that gives the best approximation to an atomic wave function in the variational sense is the solution of the Hartree-Fock equation. A familiar aspect of the Hartree-Fock method is that the equations for the single-particle orbitals are rather complicated integrodifferential equations involving the nonlocal exchange potential.

In this article we consider the related question of finding an effective local, central potential that is variationally optimized. That is, we consider a central potential $V(r)$, solve the radial Schrödinger equation for the single-particle orbitals, form a Slater determinant, and calculate $\langle H\rangle$. Then $V(r)$ is to be varied to minimize $\langle H\rangle$.

A system of self-consistent equations is derived for this problem, in which $V(r)$ is the solution of a linear integral equation. It is shown that if the exchange terms in $\langle H\rangle$ are neglected, then the solution of the problem is just $V(r)=V_H(r)$ where $V_H(r)$ is the Hartree potential constructed from the atomic charge distribution. The integral equation derived is an equation for $V(r)-V_H(r)$ and can be interpreted as an equation for an effective central exchange potential.

In Sec. II the self-consistent equations for the potential will be derived. A complicating feature of the Hartree and Hartree-Fock methods is the question of angular averaging. Since the present problem is *ab initio* spherically symmetric, it should be possible to reduce the problem by eliminating the angular dependence completely. This will be described, and the purely radial equations given, in Sec. III.

It is shown in Sec. IV that $V(r)$ behaves like $-e^2/r$ for large r, so that at large distance an electron moves in the potential of the ion it leaves behind.

The results of applying the method to carbon, neon, and aluminum are given in Sec. V. The results for the total energies differ from the Hartree-Fock results by less than 0.01 Ry, although there are greater differences in the single-particle energies.

We use units such that $2m=e^2/2=\hbar=1$. Energies are then in rydbergs, and $a_0=1$.

II. GENERAL THEORY

The expectation value for the energy for a Slater determinant formed from orbitals $\phi_i(\vec{r})$ is

$$\langle H\rangle=\sum_i\int\left[|\nabla\phi_i(\vec{r})|^2-\frac{2Z}{r}|\phi_i(\vec{r})|^2\right]d\vec{r}+\sum_{i,j}\int d\vec{r}\int d\vec{r}\,'\,\phi_i(\vec{r})^*\phi_j(\vec{r}\,')^*|\vec{r}-\vec{r}\,'|^{-1}\phi_i(\vec{r})\phi_j(\vec{r}\,')$$
$$-\sum_{i,j}\int d\vec{r}\int d\vec{r}\,'\,\phi_i(\vec{r})^*\phi_j(\vec{r}\,')^*|\vec{r}-\vec{r}\,'|^{-1}\phi_j(\vec{r})\phi_i(\vec{r}\,'). \tag{2.1}$$

A spatial integration also represents a spin sum.

The single-particle orbitals are assumed to satisfy

$$-\nabla^2\phi_i+V(r)\phi_i=e_i\phi_i. \tag{2.2}$$

The variational problem to be solved is

$$\frac{\delta\langle H\rangle}{\delta V(\vec{r})}=\sum_i\int d\vec{r}\,'\frac{\delta\langle H\rangle}{\delta\phi_i(\vec{r}\,')}\frac{\delta\phi_i(\vec{r}\,')}{\delta V(\vec{r})}=0. \tag{2.3}$$

The variational derivative

$$\frac{\delta\langle H\rangle}{\delta\phi_i(\vec{r})}=-\nabla^2\phi_i^*+V_H(r)\phi_i^*-\int d\vec{r}\,'\,V_e(\vec{r},\vec{r}\,')\phi_i(\vec{r}\,')^*, \tag{2.4}$$

and is just the left-hand side of the Hartree-Fock equation. Here

$$V_H(r)=-\frac{2Z}{r}+2\sum_j\int|\vec{r}-\vec{r}\,'|^{-1}|\phi_j(\vec{r}\,')|^2d\vec{r}\,', \tag{2.5}$$

$$V_e(r,r') = 2\sum_j \phi_j(\vec{r})^* |\vec{r}-\vec{r}'|^{-1}\phi_j(\vec{r}') . \qquad (2.6)$$

The variational derivative of ϕ_i with respect to V is obtained by introducing a variation $\delta V(r)$ in $V(r)$ in the Schrödinger equation (2.2) which becomes, to first order,

$$-\nabla^2\delta\phi_i + [V(r) - e_i]\delta\phi_i = [\delta e_i - \delta V(r)]\phi_i . \qquad (2.7)$$

If the subsidiary condition that ϕ_i is to remain normalized is imposed, (2.7) has a unique solution:

$$\delta\phi_i(r) = -\int d\vec{r}'\, G_i(\vec{r},\vec{r}')\phi_i(\vec{r}')\delta V(\vec{r}') , \qquad (2.8)$$

$$G_i(\vec{r},\vec{r}') = \sum_{j\neq i} (e_j - e_i)^{-1}\phi_j(\vec{r})^*\phi_j(\vec{r}') , \qquad (2.9)$$

in the subspace orthogonal to ϕ_i. It is seen from (2.8) that

$$\frac{\delta\phi_i(\vec{r}')}{\delta V(\vec{r})} = -G_i(\vec{r}',\vec{r})\phi_i(\vec{r}) . \qquad (2.10)$$

The results (2.4) and (2.10) can now be substituted into (2.3), and, if the Schrödinger equation (2.2) is used, it is found that

$$\sum_i \int d\vec{r}' \Big([V(r') - e_i - V_H(r')]\phi_i(\vec{r}')^* + \int d\vec{r}''\, V_e(\vec{r}',\vec{r}'')\phi_i(\vec{r}'')^* \Big) G_i(\vec{r}',\vec{r})\phi_i(r) = 0 .$$

The terms in e_i in this equation are zero since $G_i(\vec{r},\vec{r}')$ projects into the subspace orthogonal to ϕ_i. The variational equation is then reduced to the final form

$$\int d\vec{r}'\, H(\vec{r},\vec{r}')[V(r') - V_H(r')] = Q(\vec{r}) , \qquad (2.11)$$

where

$$H(\vec{r},\vec{r}') = \sum_i \sum_{j\neq i} (e_j - e_i)^{-1}\phi_i(\vec{r})^*\phi_j(\vec{r})^*\phi_i(\vec{r}')\phi_j(\vec{r}') , \qquad (2.12)$$

$$Q(\vec{r}) = -\sum_i \int d\vec{r}' \int d\vec{r}''\phi_i(r)^* G_i(\vec{r},\vec{r}') \times V_e(\vec{r}',\vec{r}'')\phi_i(\vec{r}'') . \qquad (2.13)$$

The sum on j in (2.12) need be taken only over unoccupied states, since the summand is antisymmetric in i and j. It is then seen that $H(\vec{r},\vec{r}')$ is symmetric and also positive definite provided the ground-state configuration is considered.

The nature of Eq. (2.11) is now apparent. If the exchange terms in $\langle H\rangle$ had been ignored, $Q(r)$ would be zero and the unique solution of (2.11) would be $V(r) = V_H(r)$. In the actual situation, the solution of the integral equation for $V(r) - V_H(r)$ represents an effective local central exchange potential $V_{\mathrm{ex}}(r)$.

III. RADIAL EQUATIONS

In this section the problem of reducing Eqs. (2.2) and (2.11) to radial equations will be considered. For a closed-shell atom the sums over magnetic quantum numbers in Eq. (2.1) can be performed using the spherical-harmonic addition theorem. The result of the angular integrations is

$$\langle H\rangle = \sum_i n_i \int_0^\infty \left(\phi_i'(r)^2 - \frac{2Z}{r}\phi_i(r)^2\right)dr + \frac{1}{2}\sum_{ij} w_{ij}\int_0^\infty dr \int_0^\infty dr'\, \phi_i(r)^2 v_0(r,r')\phi_j(r')^2$$
$$-\frac{1}{4}\sum_{ij} w_{ij} \sum_L \begin{pmatrix} l_i & l_j & L \\ 0 & 0 & 0\end{pmatrix}^2 \int_0^\infty dr \int_0^\infty dr'\, \phi_i(r)\phi_j(r')v_L(r,r')\phi_j(r)\phi_i(r') , \qquad (3.1)$$

where $w_{ij} = n_i n_j$, n_i being the number of electrons in shell i. Also

$$v_L(r,r') = 2\,\min(r,r')^L/\max(r,r')^{L+1} \qquad (3.2)$$

and $\phi_i(r)$ is the reduced radial wave function for shell i. The sums in Eq. (3.1) are now over shells rather than single-particle states.

If the atom contains n_v valence electrons outside a closed core, the angular dependence can be removed by averaging $\langle H\rangle$ over the degenerate states of the particular configuration being considered. In Hartree-Fock calculations this averaging process has been called the hyper-Hartree-Fock method.[3] In the present calculation, no approximation is involved in doing this since the degenerate states of a configuration remain degenerate in the presence of the effective central potential. Therefore the values of $\langle H\rangle$ averaged are all the same.

It can be shown[4] (Appendix 3 of Ref. 4) that the result of performing this averaging is to replace w_{ij} by

$$w_{ij} = n_i n_j , \quad i \text{ or } j \neq v$$
$$w_{vv} = n_v(n_v - 1)V/(V-1) , \qquad (3.3)$$

where V is the number of valence states.

The variational calculation is now much the same as in Sec. II. The final result is

$$\int_0^\infty H(r,r')[V(r') - V_H(r')]\,dr' = Q(r)\,, \tag{3.4}$$

where

$$H(r,r') = \sum_i n_i \phi_i(r) G_i(r,r') \phi_i(r')\,, \tag{3.5}$$

$$V_H(r) = \sum_i n_i \int_0^\infty v_0(r,r')\phi_i(r')^2\,dr'\,, \tag{3.6}$$

$$Q(r) = -\frac{1}{2}\sum_{ij} w_{ij}\int_0^\infty dr'\,\phi_i(r)G_i(r,r')\phi_j(r')\sum_L \begin{pmatrix} l_i & l_j & L\\ 0 & 0 & 0\end{pmatrix}^2 \int_0^\infty dr''\,v_L(r',r'')\phi_i(r'')\phi_j(r'')$$
$$+\frac{n_v(n_v - V)}{V-1}\int_0^\infty dr'\,\phi_v(r)G_v(r,r')\phi_v(r')\int_0^\infty v_0(r',r'')\phi_v(r'')^2\,dr''\,. \tag{3.7}$$

The function $G_i(r,r')$ is the Green's function for the reduced radial Schrödinger equation projected into the subspace orthogonal to ϕ_i. It satisfies the equation

$$-\frac{d^2}{dr^2}G_i(r,r') + [V(r) - e_i]G_i(r,r') = \delta(r - r') - \phi_i(r)\phi_i(r')\,. \tag{3.8}$$

A symmetric solution of (3.8) is

$$G_i(r,r') = \psi_i(r_<)\phi_i(r_>) - \phi_i(r')\Psi_i(r) - \phi_i(r)\Psi_i(r') + C_i\phi_i(r)\phi_i(r')\,, \tag{3.9}$$

where ψ_i is any second solution of the homogeneous equation such that the Wronskian $\phi_i\psi_i' - \psi_i\phi_i' = 1$. Also

$$\Psi_i(r) = \phi_i(r)\int_0^r \phi_i(r')\psi_i(r')\,dr' + \psi_i(r)\int_r^\infty \phi_i(r')^2\,dr' \tag{3.10}$$

is the solution of the inhomogeneous equation (3.8) with $\phi_i(r)$ on the right-hand side.

The third and fourth terms in (3.9) are solutions of the homogeneous equation added to maintain the symmetry of $G_i(r,r')$ and the orthogonality to $\phi_i(r)$. The value of C_i is determined by the latter property to be

$$C_i = \int_0^\infty \phi_i(r)\Psi_i(r)\,dr\,. \tag{3.11}$$

It may be noted that the homogeneous equation corresponding to Eq. (3.4) has a solution $V(r) - V_H(r) = V_{\text{ex}}(r) = C$. It is therefore natural to add a further boundary condition that $V_{\text{ex}}(r) \to 0$ for $r \to \infty$. In practice, the integral was cut off at an upper limit of about $15a_0$, and this condition was fulfilled automatically. If, however, the cut-off were chosen to be too large, the integral equation, which is approximated by a system of linear equations, would become singular and it would be necessary to impose the boundary condition in another way.

IV. BEHAVIOR OF $V(r)$ FOR LARGE r

For large r, the terms in $H(r,r')$ and $Q(r)$ in Eq. (3.4) decrease exponentially and are dominated by the term contributed by the most weakly bound (valence) electron. The sums on i in Eqs. (3.6) and (3.7) then reduce to a single term ($i = v$). Equation (3.4) then is asymptotically

$$\int_0^\infty G_v(r,r')y(r')\,dr' = \int_0^\infty G_v(r,r')h(r')\,dr'\,, \tag{4.1}$$

$$y(r) = \phi_v(r)V_{\text{ex}}(r)\,, \tag{4.2}$$

$$h(r) = -(2n_v)^{-1}\sum_j w_{vj}\phi_j(r)\sum_L \begin{pmatrix} l_v & l_j & L\\ 0 & 0 & 0\end{pmatrix}^2 \int_0^\infty dr'\,v_L(r,r')\phi_v(r')\phi_j(r') + \frac{n_v(n_v - V)}{V-1}\phi_v(r)\int_0^\infty v_0(r,r')\phi_v(r')^2\,dr'\,. \tag{4.3}$$

If Eq. (4.1) is multiplied by the local differential operator $-d^2/dr^2 + V(r) - e_v$, the result is, from Eq. (3.8),

$$y(r) - h(r) - \phi_v(r)\int_0^\infty \phi_v(r')[y(r') - h(r')]\,dr' = 0\,. \tag{4.4}$$

It follows from this that $y(r) = h(r) + \lambda\phi_v(r)$ where λ is arbitrary. This arbitrariness is because of the possibility of adding a constant to $V_{\text{ex}}(r)$, but the added condition $V_{\text{ex}}(r) \to 0$ shows that $\lambda = 0$ and $y(r) = h(r)$.

For large r, the sum on j on the right-hand side

TABLE I. Total energies in rydbergs for carbon, neon, and aluminum atoms calculated with the optimized potential, the $X\alpha$ method, and the Hartree-Fock (HF) method (Ref. 5).

	C	Ne	Al
Optimum	−75.3160	−257.0899	−483.7454
$X\alpha$	−75.3072	−257.0662	−483.7224
HF	−75.3194	−257.0942	−483.7536

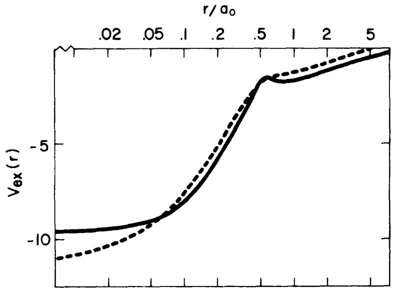

FIG. 1. Optimized effective exchange potential, solid curve, and the $X\alpha$ exchange potential, broken curve, for carbon.

of Eq. (4.3) is dominated by the term $j = v$. It can then be readily verified that the leading term for large r is given by $L = 0$ and that

$$V_{ex}(r) \approx -2/r. \tag{4.5}$$

V. RESULTS AND DISCUSSION

The radial Schrödinger equation and Eq. (3.4) have been solved numerically for the cases of carbon, neon, and aluminum atoms. The self-consistent procedure converges satisfactorily in about seven iterations if the average of the initial and final $V(r)$ is taken at each iteration. The results for the total energy are given in Table I together with the results for the hyper-Hartree-Fock calculation of Mann[5] as quoted by Slater.[4]

Another approach to the problem of an effective central local exchange potential is the $X\alpha$ method which has been espoused by Slater[4] among others. In this approach, $V_{ex}(r)$ is approximated by

$$V_{ex}(r) = -6\alpha[3\rho(r)/8\pi]^{1/3}, \tag{5.1}$$

where α is an adjustable parameter. There are various criteria for choosing α, one of which is to choose α to minimize the value of $\langle H \rangle$.[6] Other choices of α are such that the virial theorem will be satisfied or that the energy of a certain model Hamiltonian involving α will equal the exact Hartree-Fock energy. The total energies calculated for various α values differ, however, by less than 0.001 Ry.[7] The $X\alpha$ values of the total energy for the cases considered are also given in Table I. These were calculated in the same way as the energies for the optimized potential and differ slightly (by less than 0.002 Ry) from previous calculations.[7] It is seen that the optimized potential represents a substantial advance, by a factor of about 4, toward the "best" Hartree-Fock results.

The single-particle energies for the cases considered are shown in Table II. These are seen to be close to the Hartree-Fock single-particle energies for the outer electrons. This is evidently because the optimized potential has the correct asymptotic behavior for large r.

The effective exchange potentials for the three cases are shown in Figs. 1–3, together with the corresponding $X\alpha$ potentials. The r^{-1} dependence of the optimized potentials compared with the exponential dependence of the $X\alpha$ potentials is noticeable. The kinks in the optimized potential may be of interest, but there is no clear physical interpretation of them. If the potential were considered to arise from a unit positive charge dis-

TABLE II. Single-particle energies in rydbergs for carbon, neon, and aluminum, using the optimized potential, the $X\alpha$ method, and the Hartree-Fock method.[a]

Atom	Potential	$1s$	$2s$	$2p$	$3s$	$3p$
C	Optimum	−20.71	−1.45	−0.81	···	···
	$X\alpha$	−20.21	−1.00	−0.39	···	···
	HF	−22.64	−1.41	−0.86	···	···
Ne	Optimum	−61.78	−3.46	−1.72	···	···
	$X\alpha$	−61.06	−2.65	−0.99	···	···
	HF	−65.54	−3.86	−1.70	···	···
Al	Optimum	−111.4	−8.38	−5.52	−0.79	−0.43
	$X\alpha$	−111.0	−7.96	−5.21	−0.54	−0.17
	HF	−119.0	−9.82	−6.44	−0.79	−0.42

[a] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974). The energies for carbon are for the ^3P term.

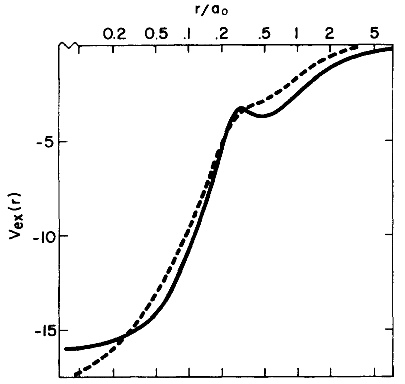

FIG. 2. Optimized effective exchange potential, solid curve, and the $X\alpha$ exchange potential, broken curve, for neon.

tributed in the atom, these would correspond to regions of negative charge.

Graphs of the total effective potential $V(r)$ show little difference from the $X\alpha$ potential. In fact, one of the conclusions of this work may be that, for a one-parameter model, the $X\alpha$ method is a remarkably good approximation. The optimized potential described here may be valuable, however, for those calculations that depend strongly on the asymptotic form of the potential.

Another variational approach to the effective atomic potential is that of Bass *et al.*[8,9] who assume a two-parameter model for the potential and adjust the parameters to minimize the total energy. The model assumed has the correct behavior for large r. The resulting potentials are also very close to the optimum, differing by at most about 0.2 for $r>0.1$. The optimized potentials are, however, somewhat less repulsive at $r=0$.

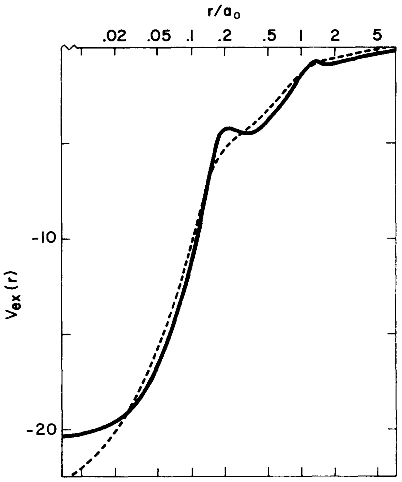

FIG. 3. Optimized effective exchange potential, solid curve, and the $X\alpha$ exchange potential, broken curve, for aluminum.

It may be of interest to note that the results for this method do not satisfy the virial theorem since the trial wave functions do not admit changes of scale. For the cases considered the kinetic energies were 75.502, 257.888, and 484.88 Ry.

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