A RELATIVISTIC PSEUDOPOTENTIAL FOR SPHERICAL SYSTEMS*

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A relativistic pseudopotential, which is an l-dependent correction to the Schrödinger radial equation, has been derived for systems with spherical symmetry. The resulting energies and the asymptotic behaviour of the wavefunctions are correct up to α^2. The pseudopotential may be applied in a straightforward way in atomic SCF and in molecular $X\alpha$ SW calculations.

1. Introduction

The relativistic corrections to the Schrödinger Hamiltonian are, in general, introduced through an expansion of the Dirac Hamiltonian in terms of powers of the fine structure constant α, and subsequent elimination of the small components of the Dirac wavefunction [1]. The resulting equation, containing terms up to α^2 and known as the Pauli equation, is then treated perturbationally considering the term proportional to α^2 as the first order perturbation. This kind of approach leads then to corrected values of energy, but the wavefunctions remain uncorrected.

Recently some work has been done on the problem of introducing the Pauli terms to the differential equation in order to obtain improved wavefunctions [2–4]. Main difficulty connected with this kind of approach is due to singularities stronger than $1/r^2$ appearing in the spin-orbit and Darwin terms. Using effective operators which are defined to reproduce certain features of the exact relativistic solutions is an alternative method for introducing relativistic corrections to the wavefunctions [5]. In the present paper we derive a relativistic

pseudopotential for one electron in a central field. The form of the pseudopotential is obtained from the requirement of a reproduction of the relativistic energies and the asymptotic behaviour of the radial wavefunctions up to the terms proportional to α^2. The resulting formulae are directly applicable in atomic SCF and molecular XαSW calculations.

2. The hydrogen-like atom

The Schrödinger radial equation for a single electron moving in a Coulomb field has the form

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} + 2E_0\right] R(r) = 0, \tag{1}$$

where l is the angular momentum quantum number, Z — the nuclear charge, and E_0 — the nonrelativistic energy. Let us consider a differential equation of the same form, i.e.

$$\left[\frac{d^2}{dr^2} - \frac{s(s-1)}{r^2} + \frac{2z}{r} - D^2\right] R(r) = 0, \tag{2}$$

with s, z, and D to be determined. The asymptotic form of $R(r)$ is

$$R(r) \sim \exp(-Dr), \quad D > 0 \tag{3}$$

if $r \to \infty$ and

$$R(r) \sim r^t, \quad t \geqslant 0, \tag{4}$$

where $t = s$ or $t = 1-s$, if $r \to 0$. Hence, values of s and D may be determined imposing a requirement upon the asymptotic behaviour of the solutions of (2). In particular, if

$$D^2 = -E(2 + \alpha^2 E) \tag{5}$$

where E is the Dirac energy of the electron, then the asymptotic form (3) of $R(r)$ is the same as in the case of the radial solutions of the Dirac equation [1]. The parameter s determines $R(r)$ for $r \to 0$. In the case of the Dirac wavefunction $t = (k^2 - \alpha^2 z^2)^{1/2}$, where $k = \varepsilon(j + 1/2)$. Here $\varepsilon = \pm 1$, and $j = l + \varepsilon/2$ is the total angular momentum quantum number. In the nonrelativistic limit $\alpha^2 Z^2$ is neglected compared to unity, so that $t = l+1$ if $\varepsilon = 1$ and $t = l$ if $\varepsilon = -1$, while for the Schrödinger equation $t = l+1$ in both cases. In order to assure the proper limit of $R(r)$ for $\alpha \to 0$ and $r \to 0$, we put

$$s = k(1 - \alpha^2 Z^2/k^2)^{1/2}. \tag{6}$$

The solutions of (2) are regular at the origin if $t = s$ in the case of $\varepsilon = 1$ and if $t = 1-s$ in the opposite case, i.e. $t = (1-\varepsilon)/2 + |s|$.

If $R(r)$ is a bounded solution of (2), then the energy of the corresponding state is determined by the condition:

$$D^2(n_r + t) = z, \tag{7}$$

where the radial quantum number $n_r = 0, 1, 2, \ldots$ is equal to the number of nodes in $R(r)$ [1]. In addition to n_r it is customary to define $N = n_r + (1+\varepsilon)/2$. If we put

$$z = Z(1 + \alpha^2 E) \tag{8}$$

then, according to (5) and (7),

$$E = \frac{1}{\alpha^2}\left[\left(1+\left(\frac{\alpha Z}{N+|s|}\right)^2\right)^{-1/2} -1\right], \tag{9}$$

i.e. is identical with the Dirac energy of the electron. If D, s and z are determined by Eqs. (5), (6), and (8) then Eq. (2) becomes

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{r} +2E+\alpha^2 W_C(r, E)\right] R(r) = 0, \tag{10}$$

where

$$W_C(r, E) = \left(E+ \frac{Z}{r}\right)^2 - \frac{k}{\alpha^2 r^2}\left[1- \sqrt{1- \frac{\alpha^2 Z^2}{k^2}}\right] \tag{11}$$

is the effective relativistic correction.

To give an interpretation of $W_C(r, E)$, let us assume that $Z\alpha \ll 1$. Then

$$W_C(r, E) = \left(E+ \frac{Z}{r}\right)^2 - \frac{1}{2k}\left(\frac{Z}{r}\right)^2 +O(\alpha^2). \tag{12}$$

The first term is the mass velocity correction, the second one is an effective potential replacing (if $l \neq 0$) the spin-orbit and (if $l = 0$) the Darwin terms. It is interesting to note that the expectation values of the second term, in the basis of the hydrogenic non-relativistic orbitals, are the same as the expectation values of the spin-orbit and Darwin operators.

3. One electron in a central field

The radial functions describing electrons in atoms are solutions of the SCF equations which are of the same form as Eq. (1), except the Coulomb attraction term $-Z/r$ being replaced by a potential function $V(r)$. We assume that the potential has the form

$$V(r) = - \frac{Z}{r}f(r), \tag{13}$$

where $f(r)$ has no singularity and for $r \rightarrow \infty$, $f(r)$ approaches to a constant value. Eq. (2) with the condition (8), accepted by analogy with the case of $-Z/r$ potential, takes the form

$$\left[\frac{d^2}{dr^2} - \frac{s_v(s_v-1)}{r^2} -2(1+\alpha^2 E)V(r)-D^2\right] R(r) = 0. \tag{14}$$

The parameter s_v determining the behaviour of $R(r)$ for $r \rightarrow 0$ is now

$$s_v = k \sqrt{1- \frac{\alpha^2 Z^2}{k^2}f(0)^2} . \tag{15}$$

Substituting (15) and (5) and assuming that $\alpha Z \ll 1$, Eq. (14) yields

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - 2V(r) + 2E + \alpha^2 W(r, E) \right] R(r) = 0, \tag{16}$$

where

$$W(r, E) = (E - V(r))^2 - \frac{1}{2k} V(r)^2 + O(\alpha^2). \tag{17}$$

The effective potentials (12) and (17) lead to a spin splitting of the orbital energies. Eq. (16) may be written as

$$[h^0(r, E_\pm) + h^k_\pm(r)] R_\pm(r) = 0 \tag{18}$$

where h^0 is the k-independent part of the operator acting on $R(r)$ in (16), $E_\pm$ and $R_\pm$ are the orbital energies and the radial functions corresponding to $j = l \pm 1/2$, respectively,

$$h^k_+ = -V(r)^2 \frac{\alpha^2}{2(l+1)}, \tag{19}$$

and

$$h^k_- = V(r)^2 \frac{\alpha^2}{2l}. \tag{20}$$

In some cases it is convenient to neglect the spin splitting of the orbitals, e.g. when one wants to introduce in a simple way the relativistic correction to an existing nonrelativistic SCF programme. For this purpose one may define an averaged operator for a shell l^n of equivalent electrons. Let, respectively, n_+ and n_- be the number of electrons for which $j = l + 1/2$ and $j = l - 1/2$. Then we define the averaged operator as

$$\overline{h} = h^0 + \frac{1}{n} (n_+ h^k_+ + n_- h^k_-). \tag{21}$$

Using (19) and (20) we obtain

$$\overline{h} = h^0 - \tfrac{1}{2} \alpha^2 V(r)^2 g(l), \tag{22}$$

where

$$g(l) = \frac{1}{n} \left(\frac{n_+}{l+1} - \frac{n_-}{l} \right). \tag{23}$$

In the special case of a closed shell ($n_+ = 2l+2, n_- = 2l$), Eq. (23) gives $g(l) = 0$ if $l \neq 0$, and $g(0) = 1$.

. The derived formulae for the relativistic pseudopotential may easily be introduced to any programme solving a radial Schrödinger equation. In particular they may be applied in the Hartree-Fock or Hartree-Fock-Slater calculations for atoms and in the SCF $X\alpha$ Scattered Wave calculations for molecules.

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