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Electromagnetic potential in Thomas-Fermi-Dirac atoms

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The authors discuss the relativistic Thomas-Fermi model for atoms and derive a relativistic extension of the Dirac exchange term. As a result of this model the mutual cancellation of the exchange and relativistic corrections to the energies of inner-shell electrons in heavy atoms ($Z > 50$) is demonstrated.

I. INTRODUCTION

The formation of quasimolecules in heavy-ion collisions[1] has stimulated interest in the calculation of relativistic molecular electronic states.[2,3] The complexity of the collision constitutes a challenge to the theory to meet the needs of the experimentalists and calculate for example the ionization degree of the inner shells.[4] Although recent progress in solving the Dirac equation[2,4] provides a satisfactory single-particle basis for such calculations, it has been recognized that the screening of molecular states by the molecular electron charge density is quite important. Recent efforts[5,6] to account for this effect have led to a revival of the Thomas-Fermi (TF) model with a shift of emphasis towards the computation of an effective local single-particle potential following from the TF-model. Such a potential should lead to a good single-particle basis when inserted into the Schrödinger or Dirac equation, in particular if exchange effects and corrections for the electronic self-interaction are included. Further, in the case of very heavy ion collisions, relativistic corrections must be taken into account too.

The first aim of the present note is to clarify the definition of the effective potential when the Dirac exchange correction (TFD model) is included. The usual way of constructing an effective single-particle potential from the TFD model, first carried through by Latter,[7] consists of the following steps: (i) the TFD equation is solved for the particular system yielding an approximation for the total electronic density $\rho(\vec{x})$ (or equivalently an approximation for the total electrostatic potential of the system), (ii) a Slater-type exchange potential[8] proportional to $\rho(\vec{x})^{1/3}$ is added, (iii) a $1/r$ behavior for large r is matched, correcting for the electronic self-interaction in the asymptotic region. In our formulation we shall derive a differential equation not for the total electrostatic but the effective potential itself; i.e., we do steps (i) and (ii) at the same time. This procedure has the advantage that certain difficulties in the traditional step (i) arising from the structure of the usual TFD equation can be avoided.

Further we include relativistic effects in the model (RTFD) and discuss the consequences of relativistic and exchange corrections for the tightly bound electron shells in heavy atoms. The mutual cancellation of the relativistic and exchange corrections, noted empirically[9] for the inner shells of heavy atoms, is proved analytically as a consequence of our approach.

Our paper is organized as follows. In Sec. II we rederive the Thomas-Fermi-Dirac Hamiltonian using a trial electronic wave function. Then, with a physical choice for the effective single-particle potential we obtain differential equations which are free of the difficulties that beset the original TFD method. For the sake of clarity we briefly illustrate these problems. Then, in Sec. III, employing the same methods we derive the RTFD equations that are considered qualitatively in Sec. IV. Throughout this paper we use the atomic unit system: lengths are measured in Bohr units [$a_0 = 137\,(\hbar/mc)$] and energies in Hartrees [$e^2/a_0 = mc^2/(137)^2$].

II. NONRELATIVISTIC THOMAS-FERMI-DIRAC MODEL

The Hamiltonian for an atom or ion with N electrons is given by the following expression:

$$H = \sum_{j=1}^{N} T_j - \sum_{j=1}^{N} W(x_j) + \tfrac{1}{2} \sum_{j,k=1}^{N} \frac{1}{|\vec{x}_j - \vec{x}_k|}\,, \tag{1}$$

where W (>0 in the present notation) denotes the Coulomb potential of the nucleus and T_j the kinetic energy of the jth electron at the point $\vec{x}_j$.

The energy E of the atom is obtained by taking the expectation value of the Hamiltonian with respect to a Slater determinant of single-particle wave functions $\phi_j(\vec{x})$:

$$E=\int\sum_{j=1}^{N}\phi_j^*(\vec{x})T\phi_j(\vec{x})\,d^3x-\int\sum_{j=1}^{N}\phi_j^*(\vec{x})W(x)\phi_j(\vec{x})\,d^3x+\tfrac{1}{2}\int\int\sum_{j,k=1}^{N}\frac{\phi_j^*(\vec{x})\phi_j(\vec{x})\phi_k^*(\vec{x}')\phi_k(\vec{x}')}{|\vec{x}-\vec{x}'|}\,d^3x\,d^3x'$$

$$-\tfrac{1}{2}\int\int\sum_{j,k=1}^{N}\frac{\phi_j(\vec{x})\phi_j^*(\vec{x}')\phi_k^*(\vec{x})\phi_k(\vec{x}')}{|\vec{x}-\vec{x}'|}\,d^3x\,d^3x'\ . \tag{2}$$

N is the number of electrons considered. In the Hartree-Fock approach the equations of motion are obtained by varying the functions $\phi_j(\vec{x})$ such as to make (2) a minimum. In order to derive the TFD energy functional we insert $T=\hat{p}^2/2m$ and assume the single-particle wave functions to be plane waves

$$\phi_j(\vec{x})=e^{i\vec{p}_j\cdot\vec{x}},\quad |\vec{p}_j|<|\vec{p}_F|\ , \tag{3}$$

where p_F is the Fermi momentum. Then we replace the discrete sum over the electron wave functions by the integral over the density of states for the plane-wave electrons, $d^3p/(2\pi)^3$. That way we obtain the well-known relation between the Fermi momentum and the total electron density

$$\rho(\vec{x})=\sum_{j=1}^{N}\phi_j^*(\vec{x})\phi_j(\vec{x})$$

$$=\frac{2}{(2\pi)^3}\int_0^{p_F}1\,d^3p=\frac{1}{3\pi^2}\,p_F^3(\vec{x})\ , \tag{4}$$

and the total energy of the N electrons now becomes:

$$E=\int d^3x\,\frac{2}{(2\pi)^3}\int_0^{p_F}\frac{p^2}{2m}\,d^3p-\int\rho(\vec{x})W(x)\,d^3x$$

$$+\tfrac{1}{2}\int\frac{\rho(\vec{x})\rho(\vec{x}')}{|\vec{x}-\vec{x}'|}\,d^3x\,d^3x'$$

$$-\frac{1}{\pi}\int d^3x\,\frac{2}{(2\pi)^3}\int_0^{p_F}p\,d^3p\ . \tag{5}$$

In view of Eq. (4), E may be considered either as a functional of $p_F(\vec{x})$ or of $\rho(\vec{x})$ only. The best ρ (or equivalently, p_F) is determined with the help of the variation principle

$$\delta[E+V_0\int\rho(\vec{x})\,d^3x]=0\ , \tag{6}$$

where V_0 is a Lagrange parameter that guarantees constant particle number. This leads to the following equation

$$c_1\rho^{2/3}-W(x)+\int\frac{\rho(\vec{x}')}{|\vec{x}-\vec{x}'|}\,d^3x'-c_2\rho^{1/3}+V_0=0\ , \tag{7}$$

where

$$c_1=(1/2m)(3\pi^2)^{2/3},\quad c_2=(3/\pi)^{1/3}\ .$$

We note that the term $-c_2\rho^{1/3}$ in Eq. (7), which originates in the exchange term of Eq. (2), has the same analytic form as the Slater exchange potential (Ref. 8). It differs from the latter only by a factor of $\frac{2}{3}$ and thus represents, according to Kohn *et al.*,[10,11] the optimal choice for an exchange potential.

As long as the density ρ is the only quantity of interest, Eq. (7) provides an integral equation for ρ. The issue we address ourselves to is to find an effective single-particle potential which will generate good electronic states when inserted into the Schrödinger or Dirac equation. Therefore we define the total effective potential $V(\vec{x})$ (>0 in our notation) as the sum of the total electrostatic and exchange potential

$$-V(\vec{x})=-W(x)+\int\frac{\rho(\vec{x}')}{|\vec{x}-\vec{x}'|}\,d^3x'-c_2\rho^{1/3}\ . \tag{8}$$

By insertion of this equation into Eq. (7) we obtain the following relation between the density and the effective potential

$$\rho=(\sigma/4\pi)(V-V_0)^{3/2},\quad \sigma=(8\sqrt{2}/3\pi)\ . \tag{9a}$$

Application of the ∇^2 operator to Eq. (8) leads, after insertion of (9a), to the new nonrelativistic TFD equation for the effective potential

$$\nabla^2V=\sigma(V-V_0)^{3/2}+\delta\nabla^2(V-V_0)^{1/2}+4\pi\rho_n,\quad \delta=\sqrt{2}/\pi, \tag{9b}$$

where ρ_n is the charge density of the nucleus. We would like to illustrate the difficulties of the usual TFD approach where the total electrostatic potential

$$-U(\vec{x})=-W(x)+\int\frac{\rho(\vec{x}')}{|\vec{x}-\vec{x}'|}\,d^3x' \tag{10}$$

is taken as the basic quantity instead of the effective potential (8). In this case one obtains by insertion of (10) into (7) and subsequent application

of ∇^2 to (10) the usual TFD equations

$$\rho = (\sigma/4\pi)[\tau + (U - V_0 + \tau^2)^{1/2}]^3 , \tag{11a}$$

$$\nabla^2 U = \sigma[\tau + (U - V_0 + \tau^2)^{1/2}]^3 + 4\pi\rho_n , \tag{11b}$$

with

$$\tau = 1/\sqrt{2}\pi .$$

In view of nonpositive roots in Eq. (11a) the density ρ is not trivially normalizable. As a consequence of this well documented[12] fact, the density as well as the potential have to be truncated at a certain critical radius.[13] These difficulties are circumvented from the very beginning by constructing a differential equation for the *effective* potential.

III. RELATIVISTIC THOMAS-FERMI-DIRAC MODEL

We start again from the Hamiltonian (1), but now we use for the kinetic energy the relativistic Dirac operator $T_j = \alpha_j \hat{p}_j + \beta_j mc^2$. As single-particle trial functions we insert the normalized wave functions for a free Dirac particle

$$\phi_j(x) = \left(\frac{E_{p_j} + mc^2}{2E_{p_j}}\right)^{1/2} \begin{pmatrix} \chi_s \\ \dfrac{\sigma \cdot p_j}{E_{p_j} + mc^2}\chi_s \end{pmatrix} e^{i\vec{p}_j(\vec{x})\vec{x}},$$

$$|\vec{p}_j| < |\vec{p}_F| , \quad E_p = (p^2c^2 + m^2c^4)^{1/2} .$$

By the same straightforward calculation as in the nonrelativistic case, we obtain now in place of Eq. (5),

$$E = \int d^3x \frac{2}{(2\pi)^3} \int_0^{p_F} (E_p - mc^2)\, d^3p - \int \rho(\vec{x}) W(x)\, d^3x + \tfrac{1}{2}\int\int \frac{\rho(\vec{x})\rho(\vec{x}')}{|\vec{x} - \vec{x}'|}\, d^3x\, d^3x' + E_x , \tag{12}$$

where the complete relativistic exchange term E_x is given by

$$E_x = -\int d^3x\, 4\pi \int_0^{p_F} \frac{d^3p}{(2\pi)^3} \int_0^{p_F} \frac{d^3p'}{(2\pi)^3} \frac{A(\vec{p}, \vec{p}')}{(\vec{p} - \vec{p}')^2} \tag{13a}$$

with

$$A(\vec{p}, \vec{p}') = \frac{1}{4E_p E_{p'}} \left((E_p + mc^2)(E_{p'} + mc^2) + 2\vec{p}\cdot\vec{p}' + \frac{p^2 p'^2}{(E_p + mc^2)(E_{p'} + mc^2)} \right).$$

Expanding the function $A(\vec{p}, \vec{p}')$ into a Taylor series for small (p/mc) (weakly relativistic approximation), one obtains up to second order

$$A(\vec{p}, \vec{p}') \cong 1 - [(\vec{p} - \vec{p}')^2/4m^2c^2] .$$

Inserting this into (13a) and evaluating the integral over d^3p', one obtains for the relativistic exchange term up to second order:

$$E_x \cong -\frac{1}{\pi} \int d^3x \frac{2}{(2\pi)^3} \int_0^{p_F} p \left[1 - \frac{1}{6}\left(\frac{p}{mc}\right)^2\right] d^3p . \tag{13b}$$

The approximation (13b) of the complete relativistic exchange term (13a) shows clearly that the relativistic energy functional (12) reduces to the nonrelativistic one for $p_F \ll mc$. Again we obtain the best ρ via the variational principle (6), which leads to the following equation:

$$(c_3\rho^{2/3} + m^2c^4)^{1/2} - mc^2 - W(x) + \int \frac{\rho(\vec{x}')}{|\vec{x} - \vec{x}'|}\, d^3x' - c_2\rho^{1/3} + c_4\rho = 0, \tag{14}$$

where $c_3 = (3\pi^2)^{2/3}$ and $c_4 = \pi/2(mc)^2$. We define as the effective relativistic TFD potential

$$-V(\vec{x}) = -W(x) + \int \frac{\rho(\vec{x}')}{|\vec{x} - \vec{x}'|}\, d^3x' - c_2\rho^{1/3} + c_4\rho \tag{15}$$

which leads us to the relativistic analog of Eq. (10)

$$\rho = (\sigma/4\pi)[(V - V_0) + (V - V_0)^2/2mc^2]^{3/2} \tag{16a}$$

$$\nabla^2 V = \sigma[(V - V_0) + (V - V_0)^2/2mc^2]^{3/2} + \delta\nabla^2[(V - V_0) + (V - V_0)^2/2mc^2]^{1/2} + \gamma\nabla^2[(V - V_0) + (V - V_0)^2/2mc^2]^{3/2} + 4\pi\rho_n \tag{16b}$$

with $\gamma = c_4\sigma/4\pi$; see also Eqs. (9) and (14). These are the relativistic Thomas-Fermi-Dirac equations.

IV. DISCUSSION AND CONSEQUENCES OF THE RTFD MODEL

In the following, we address our interest especially to the inner shells of heavy atoms where the relativistic corrections are expected to be important. The energy spectra of heavy atoms obtained from a simple nonrelativistic TF potential[9] show a better agreement than could be expected in the energy eigenvalues for inner shells obtained from relativistic Hartree-Fock-Slater

(RHFS) calculations.[14] We thus recognize that the *relativistic correction and the exchange correction cancel each other for the inner shells of heavy atoms.* We expect that the same will happen for the inner quasimolecular shells in heavy-ion collisions. In the remaining part of this paper we give qualitative reasons for the validity of this result. In doing so, we establish qualitatively the equivalence of our RTFD model with RHFS calculations.

For simplicity, we consider only the case of a neutral atom, where V_0 can be shown to be zero.[12] Furthermore we restrict ourselves to the first relativistic correction

$$(V+V^2/2mc^2)^{n/2} \cong V^{n/2} + \tfrac{1}{2}n(V^{(n+2)/2}/2mc^2), \quad n=1 \text{ or } 3 \tag{17}$$

which is a valid approximation for the inner shells of atoms with $Z < 130$. Under these restrictions, Eq. (16b) assumes the following form

$$\nabla^2 V = \sigma V^{3/2} + (3\sigma/4mc^2)V^{5/2} + \delta\nabla^2 V^{1/2} + (\gamma + \delta/4mc^2)\nabla^2 V^{3/2} + (3\gamma/4mc^2)\nabla^2 V^{5/2}] + 4\pi\rho_n \ . \tag{18}$$

For the inner shells of an atom we can approximate the RTFD potential by the expression (see March[15])

$$V(r) = Z/r - 1.79Z^{4/3} \ . \tag{19}$$

With this approximative *Ansatz* we can show that for any particular Z there exists a distance $r_0(Z)$ for which the term in square brackets in Eq. (18) vanishes, i.e., for any particular Z there exists a distance $r_0(Z)$ where relativistic and exchange effects cancel each other. In Fig. 1, we show r_0 as a function of Z. The dashed curves denote the range $\langle r\rangle \pm \Delta r$ of the Schrödinger $1s$ electronic wave function $\psi_{1s} = 2\,(-2E)^{3/4} \cdot e^{-(-2E)^{1/2}r}$, where we insert the corrected eigenenergy $E = -\frac{1}{2}Z^2 + 1.79Z^{4/3}$. The cancellation of the exchange and relativistic effects for the $1s$ shell thus occurs for atoms with $58 \lesssim Z \lesssim 85$.

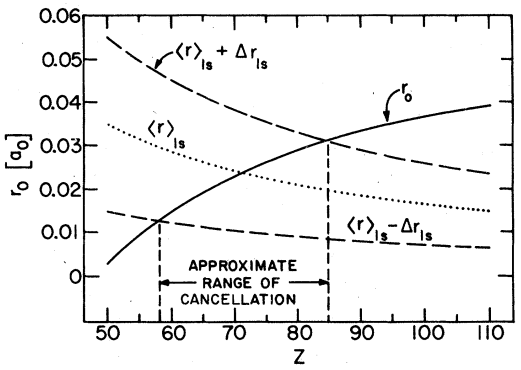

FIG. 1. Radius r_0 of cancellation between relativistic and exchange corrections as a function of the nuclear charge Z. Dotted, the expectation value $\langle r\rangle$ of the $1s$ wave function; dashed, $\langle r\rangle \pm \Delta r$.

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