

Relativistic extension of the Hohenberg-Kohn theorem

S N DATTA

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India

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Abstract. Using the configuration-space Hamiltonian H_+ which is derivable within the framework of quantum electrodynamics, we extend the Hohenberg-Kohn theorem to the relativistic theory of electrons in atoms or molecules.

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1. Introduction

Many authors (Rajagopal and Callaway 1973; Rajagopal 1978; Ramana and Rajagopal 1979; MacDonald and Vosko 1979) have formulated the relativistic density functional theory (DFT) and used it to discuss simplified systems like the electron gas. They have expressed the expectation value of the (field-theoretical) Hamiltonian as a functional of the four-current (and charge) density,

$$\langle H \rangle = E_{A_{\mu\nu}} [J_\mu]. \quad (1)$$

The four-current (and charge) density is given by

$$J_\mu(\mathbf{r}) = e \langle : \bar{\psi}(\mathbf{r}) \gamma_\mu \psi(\mathbf{r}) : \rangle. \quad (2)$$

To our knowledge, all these formulations depend on the assumption that the correct J_μ minimizes $E_{A_{\mu\nu}}$ and yields the energy of the ground state; (of course, the minimization is subject to the conditions that $\partial^\mu J_\mu = 0$ and that the total number of electrons remains constant). In other words, it is assumed that the Hamiltonian possesses a ground state (Rajagopal 1979; see also Xing-Xu *et al* 1984). With this assumption the (non-relativistic) Hohenberg-Kohn theorem (Hohenberg and Kohn 1964) is readily extended to the relativistic case.

Now, there are two problems connected with relativistic quantum chemical calculations using the linear expansion technique (Schwarz and Wallmeier 1982): (i) one needs a relativistic Hamiltonian which has at least a partially discrete eigenvalue spectrum, (the Dirac-Coulomb Hamiltonian suffers from continuum dissolution) and (ii) calculations based on usual relativistic Hamiltonians are not always safe from variational collapse (a term that is commonly used to describe a finite basis set effect). The first difficulty is usually waived by relying on projected Hamiltonians derived from

QED (Brown and Ravenhall 1951; Sucher 1980; Mittleman 1981). However, the second difficulty remains. To solve the problem, various methodologies have been recently developed (Datta 1980, 1984; Datta and Devaiah 1986; Datta and Jagannathan 1984; Gazdy and Ladanyi 1984; Mark and Schwarz 1982; Lee and McLean 1982; Wood *et al* 1985).

Actually, all previous treatments of the relativistic DFT have in one way or another taken cognizance of the first difficulty, that is, certain safeguards have been built into those treatments. Regarding the second difficulty, most of the theoretical work employ a filled negative-energy sea (see Rajagopal 1979 for a detailed discussion). From a calculational point of view the second difficulty can be really serious sometimes; this is illustrated in §2. In §3 we consider a configuration-space Hamiltonian which is derivable (Sucher 1980) within the framework of quantum electrodynamics and use it to extend the Hohenberg-Kohn theorem to the relativistic case.

2. Illustration

We use the set of trial spinors

$$\Psi_n = (1 + \lambda_n^2)^{-1/2} \begin{bmatrix} s_n \\ 0 \\ \frac{i\lambda_n}{3^{1/2}} \begin{pmatrix} p_{zn} \\ p_{xn} + ip_{yn} \end{pmatrix} \end{bmatrix}, \quad (n=1, 2, \dots), \quad (3)$$

where the nonrelativistic orbitals s_n , p_{xn} , p_{yn} and p_{zn} are described by the same radial function:

$$R_n(r) = (2\zeta_n)^{n+1/2} (2n!)^{-1/2} r^{n-1} \exp[-\zeta_n r], \quad (n=1, 2, 3, \dots).$$

Expectation values of the external field Dirac Hamiltonian for a one-electron atom ($H_{D, \text{ext}}$) are calculated. Further, $\langle H_{D, \text{ext}} \rangle_n$ is optimized through a mini-max procedure (maximum with respect to λ_n , minimum with respect to ζ_n) (Datta 1984). For every n , the optimized value equals the least eigenvalue of positive energy, that is,

$$\min_{\zeta_n} \max_{\lambda_n} \langle H_{D, \text{ext}} \rangle_n = c^2 \eta,$$

where $\eta = (1 - Z^2/c^2)^{1/2}$, $Z|e|$ being the nuclear charge. The corresponding (optimum) parameters are:

$$\lambda_{n, \text{opt}} = \lambda^0 = \frac{c}{Z} (1 - \eta) \quad \text{and} \quad \zeta_{n, \text{opt}} = 2nc\lambda^0.$$

Optimal radial densities are shown in figure 1. Corresponding four-current (and charge) densities are given by

$$e\rho_n = c^{-1} J_{n,0} = es_n^2 \quad \text{and} \quad J_n = \frac{2\lambda}{1 + \lambda^2} J_{n,0} n_{xy}$$

where $n_{xy} = (-iy + jx)/r$, for $n=1, 2, 3, \dots$. That for each n the four-vector J_μ produces

the same minimum energy [$\min_{\zeta_n} \langle H_{D, \text{ext}} \rangle_n^{\Lambda_0} = c^2 \eta$] indicates that the relativistic density functional treatment even for a one-electron atom can be ambiguous in practice.

In fact, Cortona *et al* (1985) have extended the von Barth-Hedin (1972) local-spin-density theory to the relativistic treatment of the rare-earth ions and numerically solved the resulting coupled Dirac equations. The numerical approach to solving wave equations has always been very successful (Desclaux 1973, 1975). This is so since the angular behaviour of a relativistic atomic orbital is precisely known and the corresponding radial components can be easily estimated. On the contrary, the numerical method of solving wave equation is computationally intractable for almost all molecular systems. Besides, the Hohenberg-Kohn theorem itself is based on arguments of analytical calculations, and most of the density functional calculations are performed in the same spirit.

3. A relativistic extension of the Hohenberg-Kohn theorem

An approach to the relativistic Hohenberg-Kohn theorem can start from the configuration-space Hamiltonian H_+ suggested by Sucher (1980)

$$H_+ = \sum_{i=1}^N H_{D, \text{free}}(i) + \Lambda_+ \left[e \sum_{i=1}^N \{ A_{\text{ext}}^0(\mathbf{r}_i) - \alpha_i \cdot A_{\text{ext}}(\mathbf{r}_i) \} + \sum_{i < j} \frac{e^2}{r_{ij}} \right] \Lambda_+, \quad (4)$$

where

$$\Lambda_+ = \prod_{i=1}^N \Lambda_+(i) \quad \text{and} \quad \Lambda_+(i) = \sum_{\alpha} |u_{\alpha}(i)\rangle \langle u_{\alpha}(i)|, \quad u_{\alpha}(i)$$

being a positive-energy eigenfunction of the free-particle Dirac Hamiltonian, $H_{D, \text{free}}(i)$. The Hamiltonian H_+ is not bounded from below. Therefore, one must require that the many-electron wave function $\Psi(1 \dots N)$ be constrained by

$$\Lambda_+(i) \Psi(1 \dots N) = \Psi(1 \dots N) \quad [i = 1, 2, \dots, N], \quad (5)$$

so that the minimum of $\langle H_+ \rangle$ can act as an upper bound. However, the task of relating $J_{\mu}(r)$ with a Ψ constrained by (5) is not a trivial one.

Actually, the problem of finding a good Ψ is solved in case the upper and the lower components of the spinors are decoupled. A convenient way to do so is to use a free-particle Foldy-Wouthuysen transformation (Foldy and Wouthuysen 1950) on H_+ . The positive energy part of the transformed Hamiltonian is written as (Sucher 1980; Hess 1986):

$$\hat{H}_+ = \sum_i \hat{E}_i + \sum_i \hat{V}_{\text{eff}}(i) + \sum_{i < j} \hat{U}_{\text{eff}}(i, j), \quad (6)$$

where $\hat{E}_i = (c^2 p_i^2 + m^2 c^4)^{1/2}, \quad (7)$

$$\hat{V}_{\text{eff}}(i) = -e \hat{A}_i [A_{\text{ext}}^0(i) + \hat{R}_i A_{\text{ext}}^0(i) \hat{R}_i - \hat{R}_i \sigma_i \cdot A_{\text{ext}}(i) - \sigma_i \cdot A_{\text{ext}}(i) \hat{R}_i] \hat{A}_i,$$

and

$$\begin{aligned} \hat{U}_{\text{eff}}(i, j) = & \hat{A}_i \hat{A}_j [e^2/r_{ij} + \hat{R}_i (e^2/r_{ij}) \hat{R}_i + \hat{R}_j (e^2/r_{ij}) \hat{R}_j \\ & + \hat{R}_i \hat{R}_j (e^2/r_{ij}) \hat{R}_i \hat{R}_j] \hat{A}_i \hat{A}_j. \end{aligned}$$

In (7), $\hat{A}_i = [mc^2 + E_i]/2E_i^{1/2}$ and $\hat{R}_i = [c/(E_i + mc^2)]\sigma_i \cdot p_i$. The four-current (and charge) density is rewritten as

$$J_0(\mathbf{r}_1) = ecN \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Phi^+(\mathbf{r}_1 \dots \mathbf{r}_N) \Phi(\mathbf{r}_1 \dots \mathbf{r}_N) \quad (7a)$$

and

$$J_\mu(\mathbf{r}_1) = ec^2N \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Phi^+(\mathbf{r}_1 \dots \mathbf{r}_N) \frac{p_{1\mu}}{E_1} \Phi(\mathbf{r}_1 \dots \mathbf{r}_N), \quad (\mu = 1, 2, 3), \quad (7b)$$

where Φ is the many-electron wavefunction in the new representation.

The operator \hat{H}_+ can be used to extend the Hohenberg-Kohn theorem to the relativistic problem. We see that the expectation value of

$$\sum_i \hat{E}_i + \sum_{i < j} \hat{U}_{\text{eff}}(i, j)$$

is a universal functional of $J_\mu(\mathbf{r})$, written as $F_{\text{rel}}[J_\mu(\mathbf{r})]$. Since \hat{H}_+ has a least value among its eigenvalues, it can be easily proved (by reductio ad absurdum) that to an additive constant $V_{\text{eff}}(\mathbf{r})$ is a unique functional of the ground state $J_\mu(\mathbf{r})$. Now, $V_{\text{eff}}(\mathbf{r})$ is written in terms of the four-potential and the operators \hat{A}_i and \hat{R}_i . The latter operators (\hat{A}_i and \hat{R}_i) appear through the free-particle Foldy-Wouthuysen transformation, and remain unchanged for various four-potentials. (These will change only if the nature of the transformation changes). Therefore, there is a one-to-one correspondence between $V_{\text{eff}}(\mathbf{r})$ and the four-potential. We conclude that the four-potential is a unique functional of the ground state (single particle) 4-current (and charge) density. We write

$$F_{\text{rel}}[J_\mu(\mathbf{r})] = \left\langle \Psi \left| \sum_i (mc^2 \beta_i + c \alpha_i \cdot p_i) + \sum_{i < j} \frac{e^2}{r_{ij}} \right| \Psi \right\rangle$$

(old representation) and

$$F_{\text{rel}}[J_\mu(\mathbf{r})] = \left\langle \Phi \left| \sum_i \hat{E}_i + \sum_{i < j} \hat{U}_{\text{eff}}(i, j) \right| \Phi \right\rangle$$

(new representation). For a given (external) four-potential, the ground-state energy functional is

$$E_{A_{\text{ext}}^\mu}[J_\mu] = -\frac{1}{c} \int d^3r J_\mu(\mathbf{r}) A_{\text{ext}}^\mu(\mathbf{r}) + F_{\text{rel}}[J_\mu(\mathbf{r})] \quad (\text{old representation}), \quad (8a)$$

or

$$E_{V_{\text{eff}}}[J_\mu] = V[J_\mu(\mathbf{r})] + F_{\text{rel}}[J_\mu(\mathbf{r})] \quad (\text{new representation}), \quad (8b)$$

where $V[J_\mu(\mathbf{r})] = \langle \Phi | V_{\text{eff}}(\mathbf{r}) | \Phi \rangle$. It is easily checked [from (2) or (7)] that for a normalized many-electron wave-function [Ψ or Φ] the total number of particles is a constant,

$$N[J_0] = e^{-1} c^{-1} \int d^3r J_0(\mathbf{r}) = N. \quad (9)$$

Energy as a functional of a trial state $|\Phi'\rangle$ is written as $E_{V_{err}}[|\Phi'\rangle]$. It is minimized when $|\Phi'\rangle$ is the correct ground state $|\Phi\rangle$. If $|\Phi''\rangle$ is the ground state associated with a distinctly different four-potential (one which is not obtained from the given four-potential through a gauge transformation), then

$$E_{V_{err}}[|\Phi''\rangle] = V[J''_\mu] + F_{rel}[J''_\mu] \quad \rangle$$

$$E_{V_{err}}[|\Phi\rangle] = V[J_\mu] + F_{rel}[J_\mu]. \tag{10}$$

Thus the correct $J_\mu(r)$ minimizes the ground-state energy $E_{V_{err}}$ which is a unique functional of $J_\mu(r)$.

If one investigates the one-electron atom by using the trial two-component spinors $\tilde{\phi}_n$ where

$$\tilde{\phi}_n = \begin{pmatrix} s_n \\ 0 \end{pmatrix},$$

one would observe that the radial densities shown in figure 1 give different expectation values, $\langle \tilde{H}_+ \rangle$. These radial densities do not represent the optimal densities. In fact,

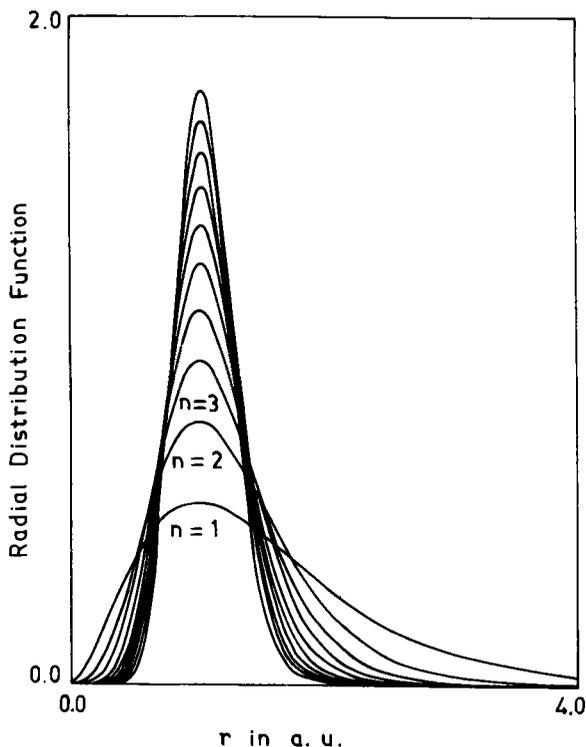


Figure 1. Radial densities which yield the same expectation value: $\langle H_{D,ex} \rangle_n = E_{1s}$ where E_{1s} is the least (positive-energy) eigenvalue of the Hamiltonian for the Dirac hydrogen atom.

the latter correspond to the new optimum parameters:

$$\zeta_{n, \text{opt}} = \left(2 - \frac{1}{n}\right) Z + O(c^{-2}),$$

with the optimized values:

$$\langle \tilde{H}_+ \rangle_{n, \text{opt}} = c^2 - \left(\frac{1}{n} - \frac{1}{2n^2}\right) Z^2 + O(c^{-2}).$$

This indicates that the minimum of $\langle \tilde{H}_+ \rangle$ will be achieved from a unique density, that is, using \tilde{H}_+ one can practice the relativistic density functional treatment in an unambiguous manner.

A relativistic density functional treatment can start from the relativistic extension of the Hohenberg-Kohn theorem as discussed here. Following the work of Stanton and Havriliak (1984) on finite basis calculations using kinetic balance we conclude that the newly formulated relativistic DFT will provide an upper bound which can be in error by an amount of order c^{-4} only. Therefore, the new method can give the accurate value of relativistic correction to total energy. Moreover, Sucher's construction of H_+ (or \tilde{H}_+) opens up the possibility of systematically studying QED effects in atoms or molecules, and the DFT based on \tilde{H}_+ can be used to calculate these effects.

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