PHYSICAL REVIEW A VOLUME 36, NUMBER 10 NOVEMBER 15, 1987

Asymptotic formula far from nucleus for exchange energy density in Hartree-Fock theory of closed-shell atoms

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(Received 24 June 1987)

In Hartree-Fock theory, the exchange energy density can be expressed solely in terms of the first-order density matrix. Far from the nucleus of a closed-shell atom, idempotency of the density matrix yields the exchange energy density as the magnitude of the Coulomb energy e^2/r times the electron density ρ. Thus two lengths enter the asymptotic form in contrast to $\rho^{-1/3}$ alone of local-density theory.

Because of the interest for density-functional theory[1,2] of Slater's simplification of the Hartree-Fock method,[3] in which the exchange energy A is approximated by

$$A_{\mathrm{HFS}} = -c_e \int \rho^{4/3} d\mathbf{r}, \quad c_e = \frac{3e^2}{4}\left[\frac{3}{\pi}\right]^{1/3} \tag{1}$$

with $\rho(\mathbf{r})$ the electron density, it remains of significance to study the exact Hartree-Fock expression for the exchange energy, which can be traced back to the work of Dirac.[4] In terms of the density matrix $\rho(\mathbf{r},\mathbf{r}_0)$, this takes the form

$$A = \frac{-e^2}{4}\int \frac{\rho(\mathbf{r}\mathbf{r}_0)\rho(\mathbf{r}_0 r)}{|\mathbf{r}-\mathbf{r}_0|} d\mathbf{r}\, d\mathbf{r}_0 \; . \tag{2}$$

From the expression (2) one can write for the exchange energy density $\epsilon_x(\mathbf{r})$, related to A by

$$A = \int \epsilon_x(\mathbf{r}) d\mathbf{r} \; , \tag{3}$$

the exact expression in the Hartree-Fock theory

$$\epsilon_x(\mathbf{r}) = \frac{-e^2}{4}\int \frac{\rho(\mathbf{r}\mathbf{r}_0)\rho(\mathbf{r}_0\mathbf{r})}{|\mathbf{r}-\mathbf{r}_0|} d\mathbf{r}_0 \; . \tag{4}$$

This expression (4) can be evaluated in two model problems. These are (i) the uniform electron gas in which the density matrix has the closed form

$$\rho_0(\mathbf{r}\mathbf{r}_0) = \frac{k_f^3}{\pi^2}\,\frac{j_1(k_f\,|\mathbf{r}-\mathbf{r}_0|)}{k_f\,|\mathbf{r}-\mathbf{r}_0|} \; , \tag{5}$$

where $j_1(x)$ is the first-order spherical Bessel function $(\sin x\text{-}x\cos x)/x^2$, while k_f is the Fermi wave number related to the uniform density $\rho_0(\mathbf{r}\mathbf{r}) \equiv \rho_0$ by the usual formula

$$\rho_0 = \frac{k_f^3}{3\pi^2} \tag{6}$$

and (ii) the Bardeen model of a metal surface.[5] In this model, the density matrix has been evaluated analytically by Moore and March,[6] and their result has been utilized by Miglio *et al.*[7] to calculate the exchange energy density.

However, while no such completely analytical results seem presently possible for the density matrix of closed-shell atoms, we can utilize the exponential decay of the Hartree-Fock wave functions far from the nucleus to make an approximate evaluation of Eq. (4) in the asymptotic limit $r \to \infty$, far from the atomic nucleus. The key result in permitting this asymptotic evaluation is the idempotency of the Dirac density matrix $\rho(\mathbf{r}\mathbf{r}_0)$, following directly from the orthonormality of the exact one-electron Hartree-Fock wave functions. Then, for sufficiently large r, the exponential decay of the wave functions ensures that the integral (4) is not dominated by the point $\mathbf{r}_0 = \mathbf{r}$ and one can write

$$\lim_{r\to\infty} \epsilon_x(\mathbf{r}) \simeq \frac{-e^2}{4r}\int \rho(\mathbf{r}\mathbf{r}_0)\rho(\mathbf{r}_0\mathbf{r}) d\mathbf{r}_0 \; . \tag{7}$$

But the idempotency of $\rho(\mathbf{r}\mathbf{r}_0)$ yields, for paired spins,

$$2\rho(\mathbf{r}) = \int \rho(\mathbf{r}\mathbf{r}_0)\rho(\mathbf{r}_0\mathbf{r}) d\mathbf{r}_0 \; , \tag{8}$$

which is, in fact, true for all $\mathbf{r}$. Substitution of Eq. (8) into Eq. (7) yields then

$$\lim_{r\to\infty} \epsilon_x(\mathbf{r}) \simeq \frac{-e^2}{2r}\rho(\mathbf{r}) \; . \tag{9}$$

Hence, in this asymptotic limit, the exchange energy density is determined in absolute magnitude by the product of the Coulomb potential energy e^2/r and the electron density $\rho(\mathbf{r})$.

Clearly, Eq. (1) would lead to the different result $-c_e\rho^{4/3}(\mathbf{r})$, and it should occasion no surprise that Slater's simplification of the Hartree-Fock method, though still valuable for estimating the total exchange energy through A_{HFS} in Eq. (1), is not appropriate, based as it is on the uniform electron gas [example (i) above], in regions far from the nucleus of an atom where the density $\rho(\mathbf{r})$ is decaying exponentially with increasing distance.

In summary, the asymptotic form embodied in Eq. (9) is the main result of this work. If one wishes, one can utilize in Eq. (9) the asymptotic formula of Pucci and

March,[8] that in Hartree-Fock theory the ratio of $\rho(r)$ to its s-state component $\rho_s(r)$ is given by

$$\rho_s(r) \sim \left[\frac{A_s}{A} \right] r^{-4} a_0^4 \rho(r), \quad a_0 = \frac{\hbar^2}{me^2} \tag{10}$$

where A_s and A are measures of the amplitudes of the asymptotic decay of ρ_s and ρ, respectively, at large r. Therefore, combining Eqs. (9) and (10), one may conclude that the r space dependence of $\epsilon_x(\mathbf{r})$ at large r could be simulated by a local-density dependence of the form $\rho(r)^{3/4}\ \rho_s(r)^{1/4}$. However, there is, of course, no assurance that the factor multiplying such a local electron density dependence will not vary strongly from atom to atom. The result (9) appears therefore to be the physically significant asymptotic form to emphasize. This plainly involves two lengths, r itself as well as $[\rho(\mathbf{r})]^{-1/3}$, in contrast to Dirac-Slater local-density theory involving only the second of these lengths. It is worth adding that at the nucleus, $\epsilon_x(0)$ is determined solely by $\rho_s(0)$ in the Dirac-Slater local-density approximation, whereas the Hartree-Fock $\epsilon_x(r=0)$, though involving again only the s-state wave functions, requires nonlocal information also about these.

It is a pleasure to acknowledge valuable discussions on Hartree-Fock theory with Dr. G. Senatore of the International Center for Theoretical Physics, Trieste. Some of this work was carried out while the author was visiting the University of California at Santa Barbara, which was supported in part by the Leverhulme Trustees, to whom the author's thanks are due.

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