

system. This method will be referred to as the HFKS method. It involves a local effective exchange potential $V_X = \delta E_X[n]/\delta n(\mathbf{r})$ where the effective exchange energy E_X is a universal functional of the electron density $n(\mathbf{r})$. Only approximate forms of E_X and V_X are known. The Kohn and Sham approximation V_{XKS} ($= 2/3$ Slater's potential) is valid for electron systems with slowly varying density (as in heavy atoms) but cannot be used in principle in band calculations where wave numbers q larger than k_F are quite significant (Geldart and Vosko 1966).

The HF test particle static dielectric function $\epsilon(q)$ and the HF electron dielectric function $\tilde{\epsilon}(q)$ of a homogeneous electron gas (Kleinman 1967, Shaw 1970) are directly related to the HF density response to an external potential. They are exactly given by the linearized HFKS equations, since the Kohn and Sham method allows an exact calculation of the ground state HF energy functional and its derivatives, such as the density and the Fermi level. A simple calculation (Harrison 1969) gives

$$\epsilon(q) = 1 + \frac{v(q)\pi_0(q)}{1 + X(q)\pi_0(q)} \quad (1)$$

$$\tilde{\epsilon}(q) = 1 + \{v(q) + X(q)\}\pi_0(q) \quad (2)$$

where $v(q)$ is the direct interaction function $4\pi e^2/q^2$, $\pi_0(q)$ the RPA static screening function and $X(q)$ the effective exchange interaction defined by equation (5) below.

We use a new variational method for $E_X[n]$ (Dagens 1971; this paper will be referred to as I), to derive an upper bound for $X(q)$ and, as a consequence, a lower bound for $\epsilon(q)$ and upper bound for $\tilde{\epsilon}(q)$, which are exact in the HF scheme.

An inequality verified by $E_X[n]$ is given first. The derivation is given in I. The exact solution of the HFKS equation is known to be a functional $\phi_k[n]$ of $n(\mathbf{r})$ (Hohenberg and Kohn 1964) which satisfies identically equation (3). Let $\psi_k[n]$ be a trial wave function which satisfies

$$\sum_{k\sigma}^{\text{occ}} |\psi_k[n]|^2 \equiv n \equiv \sum_{k\sigma}^{\text{occ}} |\phi_k[n]|^2. \quad (3)$$

We denote by $\mathcal{E}_X\{\psi_k\}$ the well known expression of the true exchange energy and by $T\{\psi_k\}$ the total kinetic energy. The fundamental formula is then

$$E_X[n] \leq \mathcal{E}_X\{\psi_k[n]\} + T\{\psi_k[n]\} - T\{\phi_k[n]\}. \quad (4)$$

The equality is obtained when the trial wave function is identical (as a functional of n) to the exact HF wave function. The second member is then stationary. It must be noted that the value of E_X is generally not equal to the true exchange energy.

We consider an electron gas perturbed by a small external potential $\lambda V_0(\mathbf{r})$. The effective exchange energy $E_X[n]$ can be written (Harrison 1969) as

$$E_X[n] = E_X^0(n_0) + \frac{\Omega}{2} \sum_q' |n_q|^2 X(q) + O(\lambda^3) \quad (5)$$

where $E_X^0(n_0)$ is the exchange energy of the homogeneous system and $X(q)$ the effective exchange interaction. The summation is over all nonzero wave vectors q , and n_q is the Fourier coefficient of the density (mean value of $n(\mathbf{r}) \exp(-i\mathbf{q}\cdot\mathbf{r})$). Let $a_q(k)$ be the Fourier coefficient of $\phi_k \exp(-i\mathbf{k}\cdot\mathbf{r})$, with the following normalization

$$a_0(k)^2 = 1 - \sum_q' |a_q(k)|^2. \quad (6)$$

$a_q(k)$ and n_q are known to be first order quantities in λ . A simple calculation leads to

$$a_q(k) = \frac{2m}{\hbar^2} \frac{1}{|\mathbf{k} + \mathbf{q}|^2 - k^2} \frac{n_q}{\pi_0(q)} + O(\lambda^2) \quad (7)$$

when $q \neq 0$.

example, by comparing the calculations of Hurst (1959) for LiH with the observed structure factors, Calder *et al.* (1962) obtained $R = 0.02$ which shows an order of magnitude better agreement.

Phillips and Weiss (1969) measured the Compton profile of LiH using Mo K α X rays scattered along three different crystallographic directions. Since they did not obtain appreciable anisotropy, they averaged their results over the three directions. The Compton profile is the projection of the electron momentum distribution on the direction of the momentum transfer. It is given by

$$J(p_{0z}) = 2\pi \int_{p_{0z}}^{\infty} |\chi(p_0)|^2 p_0 dp_0 \quad (4)$$

where p_{0z} is the projection of the initial electron momentum p_0 on the momentum transfer direction z . Assuming s like wave functions, we have

$$\chi(p_0) \propto \int_0^{\infty} P(r) j_0(p_0 r) r dr \quad (5)$$

We calculated the Compton profile of LiH using equation (4) and (5), and the wave functions of Kunz. In figure 1 we compare these calculations with the experimental curve of Phillips and Weiss. It is seen again that there is marked disagreement between experiment and the wave functions calculated by Kunz.

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Bounds for the Hartree-Fock effective exchange interaction and the static dielectric constants

Abstract. We use a variational form of the Kohn and Sham general effective exchange energy to derive an upper bound for the effective exchange interaction. Exact bounds (within the Hartree-Fock scheme) are deduced for the usual (test particle) static dielectric constant and the electron-dielectric constant.

Kohn and Sham (1965) showed that a Hartree-Fock-Slater like method (Slater 1951) allows an exact calculation of the Hartree-Fock (HF) ground state energy of an electron