PHYSICAL REVIEW A VOLUME 1, NUMBER 3 MARCH 1970

Local Exchange Approximations and the Virial Theorem*

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(Received 20 October 1969)

Two contradictory conclusions on the question whether the local exchange potentials yield energy values consistent with the virial theorem are resolved here.

Recently Berrondo and Goscinski[1] have demonstrated that the kinetic and potential energies calculated from both of the proposed local exchange potentials do not satisfy the virial theorem. On the other hand, Ross[2] has earlier shown that, whereas the Slater exchange[3] does not satisfy the virial theorem, the Kohn-Sham[4] version (sometimes known as the Kohn-Sham-Gaspar[5] exchange, – though, strictly speaking, it should be called the Dirac[6] exchange) does satisfy the virial theorem. It is the purpose of this short communication to resolve the contradiction.

We shall first show that if the procedure suggested by Kohn and Sham[4] is followed completely, then the virial theorem is satisfied. Neglect correlation effects here as being irrelevant to the discussion of exchange approximations. Then, the ground-state energy of the electronic system in the presence of the nuclear potential $v(\vec{r})$ can be written as

$$E=\int v(\vec{r})\, n(\vec{r})d\vec{r} + \frac{1}{2}\iint \frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,' + T_s[n] + E_x[n] \ , \tag{1}$$

where $n(\vec{r})$ is the density distribution, $T_S[n]$ is the kinetic energy of the independent fermion system completely determined by the density distribution[7] $n(\vec{r})$ and the exchange energy $E_x[n]$.

Following the spirit of Slater's approximation,[3] Kohn and Sham keep the kinetic energy $T_S[n]$ intact and approximate the exchange part by the expression appropriate for slowly varying density

$$E_x[n] \simeq \int n(\vec{r})\epsilon_x(n(\vec{r}))d\vec{r} \ , \tag{2}$$

$$\text{where} \quad \epsilon_x(n) = -\tfrac{3}{4}(3n/\pi)^{1/3} \ . \tag{3}$$

It then follows from the variational principle with respect to the density[7,4] that the density distribution is determined by the single-particle Schrödinger equation with the potential including an exchange part of the Dirac form

$$v_x(\vec{r}) = \mu_x(n(\vec{r})) = \tfrac{4}{3}\epsilon_x(n(\vec{r})) \ . \tag{4}$$

To reach the virial theorem, let us scale the linear dimension of the system by a factor $1/\lambda$ without changing the nuclear Coulomb potential. The scaled density distribution is given by

$$n_\lambda(\vec{r}) = \lambda^3 n(\lambda\vec{r}) \ , \tag{5}$$

preserving the total number of electrons. The kinetic and potential energies are, respectively,

$$T_\lambda = T_s[n_\lambda] = \lambda^2 T_s[n] \ , \tag{6}$$

$$V_\lambda = \lambda V \ , \tag{7}$$

where

$$V=\int d\vec{r}\, n(\vec{r})\, v(\vec{r}) + \frac{1}{2}\iint \frac{n(\vec{r})n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,' + E_x[n] \ . \tag{8}$$

Equation (7) is true not only for the Hartree-Fock expression for the exchange energy but also for the approximation (2) (and, indeed, for any part of the gradient expansion). Hence, the virial theorem follows from the variational theorem

$$2T_s[n] + V = 0 \ . \tag{9}$$

This is an alternative proof to Ross's, which uses the variation of wave functions.[2] Equation (9) holds even when we determine the density using the exchange potential (4), provided we calculate the energy terms by the same approximation (2). This derivation shows clearly the close relation between the virial theorem and the variational theorem (with respect to density variation). Since the exchange potential (4) is derived from the local density approximation (2) by means of the variational theorem, it satisfies the virial theorem which is just the consequence of a special type of density variation. It is clear that we can also make the Slater exchange satisfy the virial theorem if we are willing to modify the exchange energy (2) by a factor.[2,8]

Evidently, Berrondo and Goscinski[1] have departed from the above procedure by calculating the energy as the expectation value of the exact Hamiltonian with the wave function constructed from the approximate exchange potential. Examples of both types of computation exist. Tong and Sham[9] followed the first procedure of using Eq. (2), whereas Cowan *et al.*[10] followed the second procedure. For example, Tong and Sham's value for the total energy of Ar is -1049.027 Ry, whereas the value given by Cowan *et al.* is -1053.569 Ry, which is closer to the Hartree-Fock value of -1053.613 Ry. The second procedure gives a better value for the total energy since it amounts to using the exact expression for $E_x[n]$ even though the wave function is determined by using the exchange potential derived from an approximate expression for $E_x[n]$. It is precisely this inconsistency in the use of approximations which spoils the virial theorem.

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[*] Supported in part by the National Science Foundation, Grant No. GP-14912.

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PHYSICAL REVIEW A VOLUME 1, NUMBER 3 MARCH 1970

Rotational Correlation Functions and Neutron Scattering by Symmetric Molecules[*]

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(Received 29 October 1969)

Classical rotational correlation functions for symmetric molecules are derived from quantum-mechanical results in neutron scattering. The analysis differs from an earlier calculation in that all values of the projection quantum number are considered. The results agree with those obtained by St. Pierre and Steele using classical statistical mechanics. Numerical results for ammonia and water are presented.

Recently, we discussed a method of studying slow-neutron scattering by molecular gases in terms of classical rotational correlation functions $F_l(t)$.[1] It was later pointed out by St. Pierre and Steele[2] that the symmetric rotor expression given in this work is not generally valid because the analysis considered only small values of the projection quantum number K. In this paper, we rederive $F_1(t)$ and $F_2(t)$ for symmetric molecules and obtain results which agree with those obtained by St. Pierre and Steele, who used a different approach. We also present numerical results for ammonia gas and water vapor which are in satisfactory agreement with experiment.

In dealing with neutron scattering from hydrogenous systems, the intermediate scattering function of a rigid rotor is[1]

$$\chi_r(\vec{\kappa},t)=\langle e^{i\vec{\kappa}\cdot\vec{b}(t)}\, e^{-i\vec{\kappa}\cdot\vec{b}(0)}\rangle , \tag{1}$$

where $\vec{b}(t)$ is the position vector of the rotor at time t, $\vec{\kappa}$ is the momentum transfer variable, and $\langle\cdots\rangle$ denotes a quantum-mechanical thermal average. Evaluation of Eq. (1) proceeds from the expansion