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RESEARCH NOTE

Inconsistent kinetic energy functionals of electron gases in the presence of inhomogeneous magnetic fields

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The two formally equivalent kinetic energy functionals of an electron gas in the presence of inhomogeneous magnetic fields give inconsistent results when used in a Gordon–Kim (interacting closed-shell atom) calculation. This inconsistency is a direct measure of the accuracy of the Thomas–Fermi (slowly varying potential) assumption for the system studied.

Recently we have constructed a ground state energy functional for an inhomogeneous electron gas in the presence of a weak inhomogeneous magnetic field [1]. We used the functional to calculate the nuclear magnetic shielding tensor of the $^3\Sigma_u^+$ state of H_2 [2]. The method of calculation was similar to an earlier calculation of the magnetic susceptibility tensor of $^3\Sigma_u^+ H_2$, which used the ideas of Gordon and Kim [3–5]. Both calculations lead to gauge-invariant physical quantities. In this note we point out that an alternative method for calculating the gauge-invariant kinetic energy is not consistent with our earlier method when the magnetic field is inhomogeneous and we use a Gordon–Kim type theory.

The relevant portion of the kinetic energy functional has been calculated using the following expression (for a somewhat modified version of this expression and its use in Thomas–Fermi theory see [6]):

$$T_0 \equiv -\frac{\hbar^2}{2m} 2 \int d^3\boldsymbol{r} \int_C dt \frac{e^{-iV(\boldsymbol{r})t/\hbar}}{2\pi i t} \lim_{\boldsymbol{r}' \to \boldsymbol{r}} \nabla_r^2 \langle \boldsymbol{r}t|\boldsymbol{r}'0\rangle_A, \tag{1}$$

where $V(\boldsymbol{r})$ is the effective angle particle potential, itself a function of the density of electron and magnetic field. $\langle \boldsymbol{r}t|\boldsymbol{r}'0\rangle_A$ is the single-particle propagator of a free electron in the presence of a vector potential A;

$$\langle \boldsymbol{r}t|\boldsymbol{r}'0\rangle_A \equiv \langle \boldsymbol{r}| \exp\left[\frac{it}{\hbar 2m}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2\right]|\boldsymbol{r}'\rangle. \tag{2}$$

T_0 is a functional of the density $\rho(\boldsymbol{r})$ and the magnetic field $\boldsymbol{B}(\boldsymbol{r})$. The density also depends upon the magnetic field.

T_0 is written in the form (1) because $V(\boldsymbol{r})$ (and $\rho(\boldsymbol{r})$) are assumed to vary slowly in space. Now the interacting closed shell aspect of the calculation means that for, say, two atoms [4, 5]

$$\Delta T_0 \approx T_0(\rho_A + \rho_B) - T_0(\rho_A) - T_0(\rho_B). \tag{3}$$

Suppose that we calculate T_0 using the alternative textbook method. Under the

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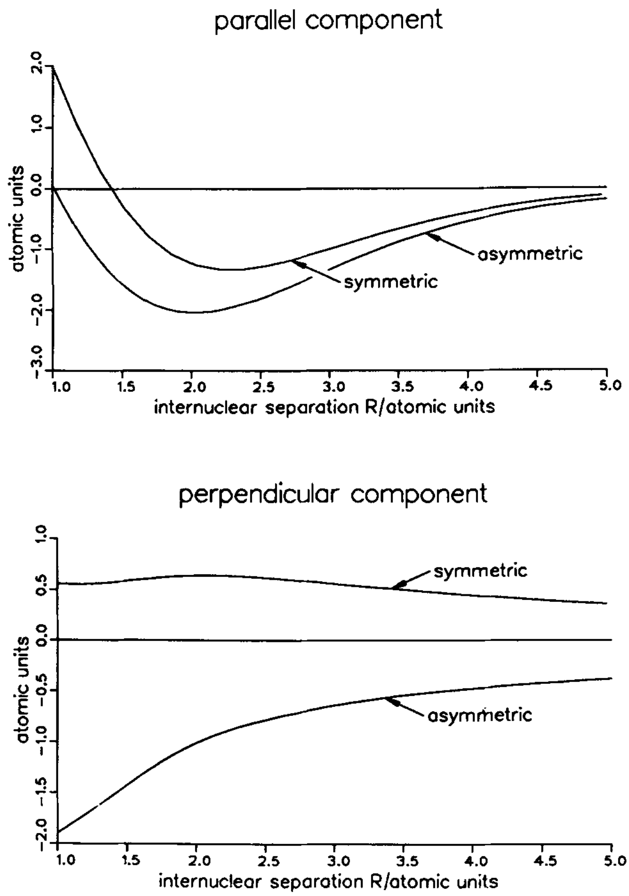

The kinetic energy contribution to the parallel and perpendicular components of the interaction nuclear magnetic shielding tensor of the $^3\Sigma_u^+$ state of H_2, shown versus internuclear separation, as calculated using the electron gas theory of [2]. The curves labelled 'asymmetric' result from the use of T_0, while those labelled 'symmetric' result from the use of T_0'.

assumptions of the last paragraph, we have

$$T_0' \equiv + \frac{\hbar^2}{2m} 2 \int \mathrm{d}^3 \boldsymbol{r} \int_C \mathrm{d}t \frac{\mathrm{e}^{-\mathrm{i}V(\boldsymbol{r})t/\hbar}}{2\pi \mathrm{i} t} \lim_{\boldsymbol{r}' \to \boldsymbol{r}} \nabla_{\boldsymbol{r}'} \cdot \nabla_{\boldsymbol{r}} \langle \boldsymbol{r}t|\boldsymbol{r}'0\rangle_A. \tag{4}$$

A priori we can see, by integrating by parts, that T_0' and T_0 differ by $\nabla V(\boldsymbol{r})$, as expected. However, when A is zero or arises from a constant or locally constant magnetic field, the two forms T_0 and T_0' are identical. This result may be shown by direct calculation. When $\boldsymbol{B}$ is inhomogeneous, such as is the case in our nuclear shielding calculations [2], the results obtained do actually differ, as may be seen in the figure.

The inconsistency described above may be looked upon as a test of the assumption of a slowly varying $V(\boldsymbol{r})$ made in the electron gas theory of interacting closed shell systems. $^3\Sigma_u^+$ H_2 is an 'electron desert', as we have said previously [2]. When the interacting systems are more elecron-rich, like ^{129}Xe, then we expect the disagreement between T_0 and T_0' to diminish.

Given the inconsistency, which form is superior? We may only give a weak answer: T_0 arises out of the natural method of expectation values and also gives more realistic results.

One final point is of interest. Although the kinetic energies are consistent when $\boldsymbol{B}$ is locally homogeneous, the exchange energy diverges [3]. This divergence cannot be corrected by a simple gradient expansion. On the other hand, treating the inhomogeneous $\boldsymbol{B}$ field 'exactly' renders the exchange energy finite. Thus we may correct for the inconsistencies in the kinetic energy by gradient expansions that do not qualitatively modify the exchange energy.

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