Löwdin correlation energy density of the inhomogeneous electron liquid in some closed-shell molecules at equilibrium geometry

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LETTER

Löwdin correlation energy density of the inhomogeneous electron liquid in some closed-shell molecules at equilibrium geometry

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Using existing theoretical studies, we point out that the dominant variable in determining Löwdin correlation energies per electron E_c/N of isoelectronic series of molecules at equilibrium is the total number of electrons. This turns out to be $E_c/N = -0.033 \pm 0.003$ a.u. for CH_4, NH_3, H_2O and HF ($N = 10$), and $E_c/N = -0.039 \pm 0.007$ for some 20 Si-containing molecules in the series SiX_nY_m. Following earlier work of March and Wind on atoms, some proposals are then made as to a possible explanation of such behaviour. A test is proposed, via low-order Møller–Plesset perturbation theory, as to whether the Löwdin correlation energy density $\epsilon_c(\mathbf{r})$ is, albeit approximately, a local functional $\epsilon_c(\rho)$ of the ground-state density for molecules at equilibrium. Such an LDA assumption would imply that $\epsilon_c(\rho)$ is quantitatively linear in $\rho(\mathbf{r})$, for closed-shell molecules at equilibrium, at least for the light atomic components treated here. This, in turn implies that the dominant effect of the Löwdin correlation energy for closed-shell molecules at equilibrium is merely to shift the chemical potential.

Keywords: correlation energy density; inhomogeneous electron liquid; closed-shell molecules

1. Introduction

The problem of correlation energy remains central in molecular physics. Here we shall take the view that in molecules and clusters in equilibrium, which we assume throughout, exchange is considerably greater than correlation, and therefore we shall assume that the Hartree–Fock (HF) theory is the appropriate starting point.

As background to the present study, we record first in Table 1 the correlation energies for electron E_c/N for $N = 10$ taken from [1]. It is clear that for these four molecules the number of electrons N is the main variable in determining the correlation energy E_c. This conclusion was reached earlier for light atoms by March and Wind [2].

To emphasise this point, Table 2 records the correlation energies per electron E_c/N for closed-shell molecules containing Si from our own earlier work [3] (see also [4]). Again,

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Table 1. Correlation energies per electron, E_c/N ($N = 10$), using many-body perturbation studies of [1].

Molecule	HF	H_2O	NH_3	CH_4
E_c (a.u.)	-0.036	-0.034	-0.032	-0.031

Table 2. Correlation energies per electron E_c/N for closed-shell molecules containing Si, ordered by increasing N [3].

Molecule	N	E_c/N (a.u.)
SiH_2	16	-0.035
SiHF	24	-0.040
SiH_3F	26	-0.038
SiF_2	32	-0.042
SiHCl	32	-0.037
SiH_2F_2	34	-0.041
SiH_3Cl	34	-0.035
$SiHF_3$	42	-0.042
SiH_2FCl	42	-0.038
$SiCl_2$	48	-0.037
SiH_2Cl_2	50	-0.036
$SiHF_2Cl$	50	-0.040
$SiHFCl_2$	58	-0.038
SiF_3Cl	58	-0.041
$SiHCl_3$	66	-0.036
SiF_2Cl_2	66	-0.039
$SiFCl_3$	74	-0.038

we see that E_c/N is rather constant for the range of molecules at equilibrium considered there. These Tables 1 and 2 have been the prime motivation for re-opening the Rayleigh–Schrödinger perturbation theory below. First, we present such a theory rather generally, and then we specialise to the case when the unperturbed solution is as given by the HF theory.

2. Proposal to test locality of correlation energy density $\epsilon_c(\mathbf{r})$ for molecules in equilibrium via low-order Møller–Plesset perturbation theory

Current software yielding the second-order Møller–Plesset (MP2) [5] correlation energy does not seem to afford the possibility to extract the correlation energy density $\epsilon_c(\mathbf{r})$ for molecules at equilibrium.

We have therefore re-opened the approach to Rayleigh–Schrödinger perturbation theory given by Young and March [6], with earlier relevant references given there. Young and March were not directly concerned with a perturbation which reflected the difference $H - H_{HF}$ between the exact Schrödinger Hamiltonian H and the Fock operator form H_{HF}. One immediate consequence of this choice of perturbation, as stressed by Møller and Plesset [5], is that the first-order perturbation energy $\langle \Psi_{HF} | H - H_{HF} | \Psi_{HF} \rangle$ is identically zero.

Of course it may be that this first-order term makes a contribution to $\epsilon_c(\mathbf{r})$, say $\epsilon_c^{(1)}(\mathbf{r})$, but this gives zero contribution to the total correlation energy $E_c = \int \epsilon_c(\mathbf{r})d\mathbf{r}$. Thus, the first contribution to E_c is $\epsilon_c^{(2)}(\mathbf{r})$, from the second-order MP correlation energy

$$E_c^{(2)} = \int \epsilon_c^{(2)}(\mathbf{r})d\mathbf{r}. \tag{1}$$

We turn therefore, first of all to the rather general Young–March formulation [6] of the first-order wave function in Rayleigh–Schrödinger perturbation theory, before specialising to the specific MP form.

Assume the unperturbed Hamiltonian is H_0, which we can take to be explicitly H_{HF}, or as recently proposed by Cabo *et al.* [7], a modified form $H_{\mathrm{m}HF}$. H_0 in either case possesses a complete orthonormal set of eigenvectors ξ_i given by

$$(E_i - H_0)\xi_i = 0. \tag{2}$$

Let us assume ξ_0 is non-degenerative and focus attention on the calculation of the corresponding ground-state eigenvalue E and eigenvector ψ given by

$$(E - H_0 - H_1)\psi = 0, \tag{3}$$

where $H_1 = H - H_0$, with H the total Schrödinger Hamiltonian involving the electron–electron interacation e^2/r_{ij}.

Then, Young and March [6] write

$$\psi = \sum_{n=0}^{\infty} K_n \xi_0 \tag{4}$$

and

$$E - E_0 = \sum_{n=0}^{\infty} \langle \xi_0 | V K_n | \xi_0 \rangle, \tag{5}$$

where in the Rayleigh–Schrödinger scheme to which we restrict ourselves here, Young and March note that

$$K_0 = 1, \tag{6a}$$

$$K_1 = \frac{1 - P}{E_0 - H_0} V, \tag{6b}$$

$$K_2 = \left(\frac{1 - P}{E_0 - H_0} V \right)^2 - \langle \xi_0 | V | \xi_0 \rangle \left(\frac{1 - P}{E_0 - H_0} \right)^2 V, \tag{6c}$$

$$\cdots \tag{6d}$$

where P is the projection operator defined by

$$P\xi_n = \xi_n \delta_{n0}. \tag{7}$$

When H_0 is either H_{HF} or $H_{\mathrm{m}HF}$, the first-order perturbation energy is identically zero. Thus, we need the first-order wave function from Equation (4), which leads one to encounter an expression of the type

$$\frac{1 - P}{E - H_0} V\xi_0 = (1 - P)\frac{1}{\epsilon - H_0} v\xi_0, \tag{8}$$

where $v = V - \langle \xi_0 | V | \xi_0 \rangle$. Young and March note that the crucial step in the evaluation of Equation (8) is to find a suitable function f such that

$$\frac{1}{\epsilon - H_0} v \xi_0 = f \xi_0. \tag{9}$$

Taking the case $H_0 = -\frac{1}{2} \sum_i \nabla_i^2 + U$, Equation (9) gives

$$(\epsilon - E_0) f + \sum_i \nabla_i f \cdot \frac{\nabla_i \xi_0}{\xi_0} + \frac{1}{2} \sum_i \nabla_i^2 f = v. \tag{10}$$

In the Rayleigh–Schrödinger form under discussion, $\epsilon = E_0$, Young and March note that in the one-particle case the method is equivalent to that introduced by Dalgarno and Lewis [8]. With this general background, we next specialise to the MP case.

2.1. Correlation energy density $\epsilon_c(r)$ within low-order MP perturbation theory

According to the general definition of Löwdin [9–11], the correlation energy or level shift E_c is defined as the difference between the exact and the HF ground-state energy, $E_c = E - E_0$.

Above we noted that the total non-relativistic Hamiltonian H is a sum of an unperturbed part H_0 and a perturbation H_1. In this section, we specialise the perturbation theory outlined above by choosing H_0 to be the HF Hamiltonian. Then we immediately have

$$H_0 \Phi_0 = E_0 \Phi_0, \tag{11}$$

where E_0 is now the HF ground-state energy and Φ_0 the corresponding (real) eigenfunction. Similarly, the exact Schrödinger equation reads for the ground state

$$H\Psi = E\Psi. \tag{12}$$

Multiplying Equation (11) on the left by Ψ and integrating over all electronic coordinates, we have

$$\int \Psi H_0 \Phi_0 \, d\tau = E_0 \int \Psi \Phi_0 \, d\tau, \tag{13}$$

where $d\tau = d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N$. Similarly, by multiplication of Equation (12) by Φ_0 and again integration over all electronic coordinates yields

$$\int \Phi_0 H\Psi \, d\tau = E \int \Phi_0 \Psi \, d\tau. \tag{14}$$

Thus, from Equations (13) and (14), see e.g. [12], we have the Löwdin correlation energy in the form

$$\begin{aligned} E_c &= \frac{\langle \Phi_0 | H | \Psi \rangle - \langle \Psi | H_0 | \Phi_0 \rangle}{\langle \Phi_0 | \Psi \rangle} \\ &= \frac{\int \Phi_0 H\Psi \, d\tau - \int \Psi H_0 \Phi_0 d\tau}{\int \Phi_0 \Psi \, d\tau}. \end{aligned} \tag{15}$$

It would be therefore natural to define a correlation energy density by omitting one integration as

$$\epsilon_c(\mathbf{r}) = \frac{\int \Phi_0 H \Psi \, d\tau' - \int \Psi H_0 \Phi_0 \, d\tau'}{\int \Phi_0 \Psi \, d\tau}, \tag{16}$$

where now $d\tau' = d\mathbf{r}_2 \cdots d\mathbf{r}_N$ and $\mathbf{r} \equiv \mathbf{r}_1$, so that

$$E_c = \int \epsilon_c(\mathbf{r}) d\mathbf{r}. \tag{17}$$

Following now Møller and Plesset [5], we assume the perturbation expansion

$$\Psi = B \left[\Phi_0 + \sum_{rs;\rho\sigma} a^{(1)}_{rs;\rho\sigma} \Phi^0_{rs;\rho\sigma} \right], \tag{18}$$

where $a^{(1)}_{rs;\rho\sigma}$ are the coefficents in the MP perturbation expansion, $\Phi^0_{rs;\rho\sigma}$ are the (orthonormal) HF excited states and B is a normalisation factor, which turns out to be

$$B = \left[1 + \sum_{rs;\rho\sigma} |a_{rs;\rho\sigma}|^2 \right]^{-1/2}. \tag{19}$$

Substitution of Equation (18) into Equation (16) then yields

$$\epsilon_c(\mathbf{r}) = (E - E_0) \left[\frac{1}{N} \rho_{\mathrm{HF}}(\mathbf{r}) + \sum_{rs;\rho\sigma} a^{(1)}_{rs;\rho\sigma} \int \Phi_0 \Phi^0_{rs;\rho\sigma} \, d\tau' \right], \tag{20}$$

where $\rho_{\mathrm{HF}}(\mathbf{r})$ is the HF density, and the remaining integrals are related to the off-diagonal elements of a HF transition-like matrix.

What must now be emphasised is that Equation (17) makes clear that $\epsilon_c(\mathbf{r})$ is not unique, since any function $f(\mathbf{r})$ can be added to $\epsilon_c(\mathbf{r})$ provided $f(\mathbf{r})$ satisfies the sum rule

$$\int f(\mathbf{r}) d\mathbf{r} = 0. \tag{21}$$

But the orthonormality of the HF wave functions Φ_0 and $\Phi^0_{rs;\rho\sigma}$ means that the last term in Equation (20) already satisfies this sum rule. Hence, we can redefine $\epsilon_c(\mathbf{r})$, denoting the new definition by $\epsilon^{\mathrm{MP}}_c(\mathbf{r})$ as

$$\epsilon^{\mathrm{MP}}_c(\mathbf{r}) = \frac{E_c}{N} \rho_{\mathrm{HF}}(\mathbf{r}). \tag{22}$$

Since we know from the MP theory that $\rho_{\mathrm{HF}}(\mathbf{r})$ is a good electron density, in the sense that it is accurate to second–order in the difference between the exact Hamiltonian and the Fock operator, we propose the semi-empirical (emp) generalisation of Equation (22) to read

$$\epsilon^{\mathrm{emp}}_c(\mathbf{r}) = \frac{E_c}{N} \rho(\mathbf{r}), \tag{23}$$

where $\rho(\mathbf{r})$ is now the exact ground-state density, while likewise E_c/N is the exact Löwdin correlation energy. Of course, Equation (23) becomes a trivial identity when integrated

over **r**, since $\int \rho(\mathbf{r})d\mathbf{r} = N$, where N is the total number of electrons in the molecule or cluster under investigation.

2.2. *Semiempirical proposal for correlation energy density for molecules and clusters at equilibrium*

Returning to the two series of molecules considered in the previous section, we could write for these the approximate formula, but now specifically at the equilibrium molecular geometry:

$$\epsilon_c^{\text{emp}}(\mathbf{r}) = (-0.034 \pm 0.003)\rho(\mathbf{r}). \tag{24}$$

What seems then remarkable to us is that the correlation energy per electron can be determined at any point **r** in the molecule or cluster, without recourse to volume integration. Thus, the present discussion leads us to the concept of a 'local' Löwdin correlation energy density. For sufficiently large distances r from all nuclei in molecules and finite clusters, the ground-state density is known to have the asymptotic form

$$\rho(\mathbf{r}) = Ar^n \exp(-2\sqrt{2I}r), \tag{25}$$

where I is the ionisation potential in astronomical units. The semi-empirical proposal, Equation (24), obviously then has the consequence that $\epsilon_c^{\text{emp}}(\mathbf{r})$ falls off exponentially at a rate governed by the ionisation potential, to be compared with the Dirac exchange energy density, which, again far from nuclei, has the asymptotic form [13]

$$\epsilon_x(\mathbf{r}) = -\frac{1}{2}\frac{e^2}{r}\rho(\mathbf{r}). \tag{26}$$

3. Summary and future directions

We have here first noted that the correlation energy per electron for two series of molecules at equilibrium recorded in Tables 1 and 2 accord with the empirical relation for the correlation energy density given in Equation (24). We have contrasted the large r behaviour of this empirical form, Equation (24), with that for the exchange energy density in Equation (26).

For the future, it will be important to attempt the construction of analytical (at first atomic) models which will allow the level-shift formula embodied in Equation (16) to be explored further within an exact, if over-simplified framework. However, the present results suggest, from Equation (24), that the main change due to correlation is to cause a shift in the chemical potential.

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