

Approximate Molecular Orbital Theory for Inorganic Molecules

IV. Electron Correlation in Molecular Orbital Calculations

R. D. BROWN and K. R. ROBY*

Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168

Received February 18, 1969/ September 29, 1969

Electron correlation is known to have an important influence on the results of molecular orbital calculations, but is not usually directly included in such calculations. An analysis of the general theory of electron correlation leads to a pair correlation hypothesis, which serves as a basis for the subsequent derivation of a way of explicitly allowing for electron correlation in the LCAOMO energy. The derived expressions carry significant implications for the semi-empirical parameter schemes of all-valence-electron methods, implying that they cannot be regarded as incorporating the correct form of correlation correction. This points to the advantage of aiming at a theoretically founded parameter scheme in approximate molecular orbital calculations, designed to produce approximate Hartree-Fock molecular wave functions. The electron correlation correction can then be applied to the expression for the total valence electron energy as developed in the present paper.

Bekanntlich hat die Elektronenkorrelation einen wichtigen Einfluß auf die Resultate von MO-Berechnungen. Sie wird jedoch gewöhnlich nicht direkt in solche Berechnungen mit einbezogen. Eine Analyse der allgemeinen Theorie der Elektronenkorrelationen führt zu einer Paar-Korrelations-hypothese, die als Grundlage für die Ableitung einer Methode dient, um die Elektronenkorrelation explizit in der LCAOMO-Energie zu berücksichtigen. Die abgeleiteten Ausdrücke wirken sich stark auf semi-empirische Parameter-Schemata von Methoden unter Einschluß aller Valenzelektronen aus, woraus folgt, daß diese keine korrekte Berücksichtigung der Korrelationskorrekturen enthalten. Es ist also vorzuziehen, theoretisch begründete Parameter-Schemata in Näherungs-MO Berechnungen anzustreben, die zu Näherungs-Hartree-Fock-Molekül-Funktionen führen sollen. Die Elektronenkorrelationskorrektur kann dann bei dem Ausdruck für die totale Valenzelektronen-Energie angewendet werden, wie es in der vorliegenden Arbeit dargestellt wird.

La corrélation électronique a une influence importante sur les résultats des calculs d'orbitales moléculaires mais n'est pas d'ordinaire incluse dans ces calculs. Une analyse de la théorie générale de la corrélation électronique conduit à une hypothèse de corrélation de paire que l'on utilise pour trouver un moyen explicite de tenir compte de la corrélation électronique dans l'énergie LCAOMO. Les expressions que l'on obtient contiennent des implications significatives pour les schéma semi-empiriques des méthodes à électrons de valence, montrant que ces méthodes ne contiennent pas la corrélation électronique sous une forme correcte. Ceci indique l'intérêt d'un schéma paramétrique théoriquement fondé dans les méthodes Hartree-Fock approchées. La correction de corrélation électronique peut alors être appliquée à l'énergie totale des électrons de valence ainsi que cela est exposé dans cet article.

1. Introduction

The necessity of making allowance for electron correlation effects in order to obtain numerical results of "chemical accuracy" (better than 1 eV) is well known [1]. In fact the correction for electron correlation may amount to as much

* Present address: Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520, USA.

as 1 eV per doubly occupied orbital [1]. Relatively few calculations of correlation energies for molecules have been reported to date but various methods are available and have been reviewed by Löwdin [2], Sinanoğlu [1] and Nesbet [3]. Here we shall follow the Sinanoğlu many-electron theory of atoms and molecules [1], writing the total many-electron wave function Ψ as a sum of Hartree-Fock and electron correlation parts:

$$\Psi = \Phi_{\text{HF}} + \Phi_{\text{corr}} \quad (1)$$

subject to the conditions

$$\langle \Phi_{\text{HF}}, \Phi_{\text{HF}} \rangle = 1, \quad \langle \Phi_{\text{HF}}, \Phi_{\text{corr}} \rangle = 0.$$

In previous parts [4–6] we set out to devise various all-valence-electron methods capable of producing approximate Hartree-Fock wave functions. We now seek an approximate correlation correction E_{corr} to be added to the Hartree-Fock energy estimated by these methods:

$$E_{\text{exact}}^{\text{non-rel}} = E_{\text{HF}} + E_{\text{corr}} \quad (2)$$

2. Pair Correlation Energies

Evidence has been mounting over recent years that the correlation energy is additive in pairs, i.e.

$$E_{\text{corr}} = \sum_{i>j} \epsilon_{ij}^{\text{corr}} \quad (3)$$

In summary the main evidence is:

(i) Intuitive; that since electrons of opposite spin are constrained to be paired in the Hartree-Fock case, the main contributions to the total correlation energy will come from these pairs.

(ii) Theoretical; in both the Sinanoğlu many-electron theory already described, and in the results of Nesbet [7] for a perturbation theory based on the superposition of configurations method, allowing only doubly excited configurations.

(iii) Semi-empirical; results of atomic Hartree-Fock calculations including relativistic corrections for series of atoms and ions when compared with experimental energies indicate that electron correlation is additive in pairs (Allen, Clementi, and Gladney [8]).

Further, such evidence indicates that, to “chemical accuracy”, only pair correlations between electrons of opposite spin in the same quantum shell are important. That is to say we may, to the first approximation, neglect correlations between electrons in different shells (intershell or “dispersion”-type correlation). It is argued (Ruedenberg [9], Salem [10]) that pair correlations between electrons of the same spin (“Fermi” correlations) are already included in the Hartree-Fock method through the quantum mechanical exchange integral ($ij|ji$).

The question of the transferability of pair correlation energies is an important one. How sensitive, for instance, are the pair correlation energies to their environment? An important distinction made by Sinanoğlu is that between “dynamical”

Table. Pair correlation energies in neutral atoms (eV)^a

	Ref.	He	Li	Be	B	C	N	O	F	Ne
<i>First row atoms</i>										
E_{corr} (total)	[13]	1.146	1.233	2.569	3.401	4.299	5.115	7.020	8.816	10.693
$\epsilon_{\text{corr}}(1s^2)$	[13]	1.146	1.184	1.205	1.219	1.227	1.233	1.238	1.241	1.243
$\epsilon_{\text{corr}}(1s-2s)$	^b		0.025	0.115	0.115	0.115	0.115	0.115	0.115	0.115
$\epsilon_{\text{corr}}(2s^2)$	[11] ^c			1.132	0.811	0.457	0	0	0	0.014
$\epsilon_{\text{corr}}(2s-2p)$					1.14	1.19	1.22	1.0	1.0	1.0
$\epsilon_{\text{corr}}(2p^2)$	^d							0.52	0.40	0.36
$\epsilon_{\text{corr}}(2p_z^2)$ est.	[11]							1.0	1.0	1.0
			Na	Mg	Al	Si	P	S	Cl	A
<i>Second row atoms</i>										
$E_{\text{corr}}(n=3)$	[14]		0.190	1.279	1.986	2.857	3.673	5.605	7.347	9.306
$\epsilon_{\text{corr}}(\text{core}-3s)$	^b		0.190	0.224	0.225	0.225	0.225	0.225	0.225	0.225
$\epsilon_{\text{corr}}(3s^2)$	[12] ^c			0.832	0.479	0.286	0	0	0	0
$\epsilon_{\text{corr}}(3s-3p)$					1.06	1.06	1.07	1.0	1.0	1.0
$\epsilon_{\text{corr}}(3p^2)$	^d							0.39	0.32	0.32
$\epsilon_{\text{corr}}(3p_z^2)$ est.	^e							0.8	0.8	0.8

^a Fermi pair correlation energies are neglected.

^b $\epsilon(1s^2-2s^2)$ and $\epsilon(\text{core}-3s^2)$ are assumed transferable across their respective rows.

^c $\epsilon_{\text{corr}}(ns^2)$ depends on the total electron population of the np orbitals. For molecular calculations, use the method of Hollister and Sinanoglu [16] to estimate this.

^d $\epsilon_{\text{corr}}(np^2)$ is an average pair correlation energy, having contributions from 'P' and 'D' pairs. This is the appropriate energy for molecular calculations when Eqs. (36) and (36A) of the text are used.

^e This work, using the method of Ref. [11] and the results of Ref. [14].

and "non-dynamical" parts of the pair correlation energies. The former are insensitive to the surrounding Hartree-Fock "sea" and consequently may be transferred from atom to atom or molecule to molecule. The latter are quite dependent on their environment.

The total correlation problem is now composed of a set of variational problems each involving only pairs of electrons. Fortunately the correlation energies $\epsilon_{\text{corr}}(1s^2)$, $\epsilon_{\text{corr}}(2p^2)$, and $\epsilon_{\text{corr}}(3p^2)$ for atoms are "dynamical" in nature and hence transferable from atom to atom [1]. However $\epsilon_{\text{corr}}(2s^2)$ and $\epsilon_{\text{corr}}(3s^2)$ are non-dynamical, varying with atomic number and decreasing along their respective rows of the Periodic Table [11, 12].

Calculated values of $\epsilon_{\text{corr}}(2s^2)$ [11] and $\epsilon_{\text{corr}}(3s^2)$ [12] may thus be used in conjunction with the total correlation energies of Clementi [13-15] to give the pair correlation energies in neutral atoms listed in the Table. In composing the Table, a number of assumptions have been made: that Fermi correlations are negligible; that the $\epsilon_{\text{corr}}(1s^2)$ and the core correlation energies of second row atoms are transferable from the He and Ne isoelectronic series, respectively; and that $\epsilon_{\text{corr}}(1s-2s)$ and $\epsilon_{\text{corr}}(\text{core}-3s)$ are transferable across their respective rows of the Periodic Table.

Another important aspect of electron correlation is apparent from the virial theorem [2], which is automatically satisfied in the Hartree-Fock approach. Thus

$$T_{\text{HF}} = -\frac{1}{2} V_{\text{HF}} = -E_{\text{HF}} \quad (4)$$

where T and V represent the total kinetic and potential energies respectively. It follows that

$$T_{\text{corr}} = -\frac{1}{2} V_{\text{corr}} = -E_{\text{corr}} \quad (5)$$

and since E_{corr} is negative, the kinetic energy correlation correction T_{corr} is positive and the potential energy correlation correction is negative. Thus T_{HF} is too low, the electrons having a more complex motion than we have allowed for, while V_{HF} is too high, correlation preventing the electrons from coming too closely together. Correlation affects both kinetic and potential energies.

We shall therefore write

$$E_{\text{corr}} = \sum_{i>j} \varepsilon_{ij}^{\text{corr}}$$

$\varepsilon_{ij}^{\text{corr}} = 0$ unless electrons i and j are of opposite spin and occupy orbitals in the same quantum shell. Then from (5)

$$\varepsilon_{ij}^{\text{corr}} = t_{ij}^{\text{corr}} + v_{ij}^{\text{corr}} \quad (6)$$

and

$$t_{ij}^{\text{corr}} = -\frac{1}{2} v_{ij}^{\text{corr}} = -\varepsilon_{ij}^{\text{corr}} \quad (7)$$

with t_{ij}^{corr} and v_{ij}^{corr} being the kinetic energy and potential energy parts, respectively, of the pair correlation energy $\varepsilon_{ij}^{\text{corr}}$.

This hypothesis receives some support, and a further possibility arises, from the work of Parr [17] and Kutzelnigg [18]. *Ab initio* calculations on the helium atom by these two authors indicate that the above virial theorem does apply in this particular case, and that the nuclear-electron interaction energy is only slightly affected by correlation. This result needs to be tested on systems containing more than two electrons, but for the time being we may use as a working hypothesis the conclusion:

The total electron correlation energy reduces to a sum of pair correlation energies. The major part of this total correlation energy arises from the motion of pairs of electrons in the same quantum shell and having opposite spin. Each separate pair correlation energy may be partitioned via the virial theorem into a correction to the kinetic energy and a correction to the potential energy of electron repulsion. The correlation is assumed, for the time being, to affect the nuclear-electron attraction energy in a negligible way.

3. Pair Correlations in the LCAOMO Method

The pair correlation hypothesis of the previous section has provided the basis for the treatment of electron correlation in molecular orbital theory. It remains to derive a way of including pair correlation energies in the energy calculated via the LCAOMO method. Starting from the pair correlation energy formula by Sinanoglu [19] for spin orbitals ψ_i and ψ_j :

$$\varepsilon_{ij}^{\text{corr}} = \frac{2\langle B(ij), m_{ij}\hat{u}_{ij} \rangle + \langle \hat{u}_{ij}, (e_i + e_j + m_{ij})\hat{u}_{ij} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} \quad (8)$$

with \widehat{u}_{ij} the pair correlation wave function, B the two electron antisymmetrizer and m_{ij} is called the "fluctuation potential" [1]. It takes the form

$$m_{ij} = \hat{g}_{ij} + (J_{ij} - K_{ij}) - (\hat{G}_j(i) + \hat{G}_i(j)) \quad (9)$$

where $\hat{G}_j(i)$ represents the Coulomb-exchange operation ($\hat{J}_j(i) - \hat{K}_j(i)$) for spin orbital j acting on electron i and \hat{J}_j and \hat{K}_j are the Coulomb and exchange repulsion operators defined by Roothaan:

$$\begin{aligned} \hat{J}_j \psi_i &= e^2 \left(\int \frac{\psi_j^*(j) \psi_j(j)}{r_{ij}} dv_j \right) \psi_i(i), \\ \hat{K}_j \psi_i &= e^2 \left(\int \frac{\psi_j^*(j) \psi_i(j)}{r_{ij}} dv_j \right) \psi_j(i). \end{aligned}$$

Finally in Eq. (8), e_i is defined by

$$e_i = \hat{F} - \varepsilon_i \quad (10)$$

where \hat{F} is the Hartree-Fock operator for the spin orbitals ψ_i , i.e.

$$(\hat{F} - \varepsilon_i) \psi_i = 0.$$

We obtain

$$\begin{aligned} e_i &= \hat{H}_{\text{core}}(i) + \hat{G}(i) - H_{ii} - \sum_{k \neq i} (J_{ik} - K_{ik}) \\ &= [\hat{H}_{\text{core}}(i) - H_{ii}] + \left[\hat{G}(i) - \sum_{k \neq i} (J_{ik} - K_{ik}) \right] \\ &= [\text{core Hamiltonian term}] + [\text{electron repulsion term}]. \end{aligned} \quad (11)$$

Since the m_{ij} of Eq. (8) involve only electron repulsion terms, we may write:

$$\begin{aligned} \langle \widehat{u}_{ij}, (e_i + e_j + m_{ij}) \widehat{u}_{ij} \rangle &= \langle \widehat{u}_{ij}, (\hat{H}_{\text{core}}(i) - H_{ii} + \hat{H}_{\text{core}}(j) - H_{jj}) \widehat{u}_{ij} \rangle \\ &+ \left\langle \widehat{u}_{ij}, \left[\hat{G}(i) - \sum_{k \neq i} (J_{ik} - K_{ik}) + \hat{G}(j) - \sum_{l \neq j} (J_{jl} - K_{jl}) + m_{ij} \right] \widehat{u}_{ij} \right\rangle \end{aligned} \quad (12)$$

In such a way, the $\varepsilon_{ij}^{\text{corr}}$ may be partitioned into two terms as follows:

$$\begin{aligned} \varepsilon_{ij}^{\text{corr}} &= \frac{\langle \widehat{u}_{ij}, [\hat{H}_{\text{core}}(i) - H_{ii} + \hat{H}_{\text{core}}(j) - H_{jj}] \widehat{u}_{ij} \rangle}{1 + \langle \widehat{u}_{ij}, \widehat{u}_{ij} \rangle} \\ &+ \left\{ 2 \langle B(ij), m_{ij} \widehat{u}_{ij} \rangle + \langle \widehat{u}_{ij}, [\hat{G}(i) - \sum_k (J_{ik} - K_{ik}) + \hat{G}(j) - \sum_k (J_{jk} - K_{jk}) + m_{ij}] \widehat{u}_{ij} \rangle \right\} \\ &\cdot \{1 + \langle \widehat{u}_{ij}, \widehat{u}_{ij} \rangle\}^{-1}. \end{aligned} \quad (13)$$

The first term is the correlation correction to the core Hamiltonian, the second the correlation correction to electron repulsion. According to the pair correlation correction hypothesis, the former is mainly a kinetic energy correction. Therefore we may write

$$\varepsilon_{ij}^{\text{corr}} = t_{ij}^{\text{corr}} + v_{ij}^{\text{corr}} \quad (14)$$

where t_{ij}^{corr} is the pair correlation kinetic energy and is identified with the first term of Eq. (13), while v_{ij}^{corr} is the pair correlation potential energy and is identified

with the second term of Eq. (13). Thus

$$\begin{aligned} E_{\text{exact}}^{\text{non-rel}} &\approx E_{\text{HF}} + \sum_i \sum_{j>i} (t_{ij}^{\text{corr}} + v_{ij}^{\text{corr}}) \\ &\approx \sum_i H_{ii} + \sum_i \sum_{j>i} (J_{ij} - K_{ij} + t_{ij}^{\text{corr}} + v_{ij}^{\text{corr}}). \end{aligned} \quad (15)$$

But

$$t_{ij}^{\text{corr}} = \frac{\langle \hat{u}_{ij}, (\hat{H}_{\text{core}}(i) - H_{ii}) \hat{u}_{ij} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} + \frac{\langle \hat{u}_{ij}, (\hat{H}_{\text{core}}(j) - H_{jj}) \hat{u}_{ij} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} \quad (16)$$

This suggests the further definition:

$$t_{ii}^{\text{corr}} = \sum_{j \neq i} \frac{\langle \hat{u}_{ij}, (\hat{H}_{\text{core}}(i) - H_{ii}) \hat{u}_{ij} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} \quad (17)$$

The pair correlation kinetic energy may be used as a correction to the core Hamiltonian matrix:

$$E_{\text{exact}}^{\text{non-rel}} \approx \sum_i (H_{ii} + t_{ii}^{\text{corr}}) + \sum_i \sum_{j>i} (J_{ij} - K_{ij} + v_{ij}^{\text{corr}}) \quad (18)$$

an important expression for the following development.

When we change from sums over occupied spin orbitals ψ_i to sums over the occupied molecular space orbitals (MO's) ϕ_i , each ϕ_i may contain two electrons having opposite spin. Factors of two accordingly appear before H_{ii} , and J_{ij} , i and j now referring to MO's. On the other hand K_{ij} applies only to electrons of like spin while $\varepsilon_{ij}^{\text{corr}}$, by the pair correlation hypothesis, applies only to electrons of opposite spin. Thus for MO's:

$$E_{\text{exact}}^{\text{non-rel}} = \sum_i (2H_{ii} + t_{ii}^{\text{corr}}) + \sum_i \sum_j (2J_{ij} - K_{ij} + v_{ij}^{\text{corr}}). \quad (19)$$

Now we introduce LCAOMO approximation:

$$\phi_i = \sum_{\mu} C_{i\mu} \chi_{\mu} \quad (20)$$

where the χ are atomic orbitals. Since $B(ij)$ is simply a two electron Slater determinant, we immediately have:

$$B(ij) = \sum_{\mu} \sum_{\nu} C_{i\mu} C_{j\nu} B(\mu\nu). \quad (21)$$

Writing Φ_{HF} as a Slater determinant of molecular orbitals ϕ_i , we apply the LCAO expansion to two of these MO's, ϕ_i and ϕ_j , for the purpose of showing how the LCAO expansion applied to the corresponding pair correlation function \hat{u}_{ij} :

$$\Phi_{\text{HF}} = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \dots \phi_i \bar{\phi}_i \phi_j \bar{\phi}_j \dots \phi_{N/2} \bar{\phi}_{N/2}| \quad (22)$$

$$\begin{aligned} &= \sum_{\mu} \sum_{\nu} C_{i\mu} C_{j\nu} |\phi_1 \bar{\phi}_1 \dots \bar{\phi}_{i\chi\mu} \bar{\phi}_i \dots \chi\nu \bar{\phi}_j \dots \phi_{N/2} \bar{\phi}_{N/2}| \\ &= \sum_{\mu} \sum_{\nu} C_{i\mu} C_{j\nu} (D_{\text{HF}})_{\mu\nu} \end{aligned} \quad (23)$$

where $(D_{\text{HF}})_{\mu\nu}$ is the Slater determinant containing χ_{μ} and χ_{ν} .

Now the definition of the exact \hat{u}_{ij} given in Ref. [1] is:

$$\hat{u}_{ij} = \left\langle \Phi'_{\text{corr}}, \frac{\Phi_{\text{HF}}}{(ij)} \right\rangle \quad (24)$$

where the Φ'_{corr} is a complex many-electron function and where $\Phi_{\text{HF}}/(ij)$ is obtained by dropping ϕ_i and ϕ_j from the Slater determinant, as below. The integration is over all electrons except the two electrons contained in ϕ_i and ϕ_j so that u_{ij} is a two-electron function. Thus we have:

$$\begin{aligned} \frac{\Phi_{\text{HF}}}{(ij)} &= |\phi_1 \bar{\phi}_1 \dots \bar{\phi}_{i-1} \bar{\phi}_i \dots \bar{\phi}_{j-1} \bar{\phi}_j \dots \phi_{N/2} \bar{\phi}_{N/2}| \\ &= \sum_{\mu} \sum_{\nu} C_{i\mu} C_{j\nu} \frac{(D_{\text{HF}})_{\mu\nu}}{(\mu\nu)} \end{aligned} \quad (25)$$

where $(D_{\text{HF}})_{\mu\nu}/(\mu\nu)$ is obtained by leaving out the pair of atomic orbitals χ_{μ} and χ_{ν} from the Slater determinant in which they occur. Then,

$$\hat{u}_{ij} = \sum_{\mu} \sum_{\nu} C_{i\mu} C_{j\nu} \hat{u}_{\mu\nu} \quad (26)$$

if we make the definition, by analogy with Eq. (24):

$$\hat{u}_{\mu\nu} = \left\langle \Phi'_{\text{corr}}, \frac{D_{\text{HF}}}{(\mu\nu)} \right\rangle. \quad (27)$$

Then, for example,

$$\begin{aligned} t_{ii}^{\text{corr}} &= \sum_{\mu} \sum_{\nu} C_{i\mu} C_{i\nu} \sum_j \sum_{\lambda} \sum_{\sigma} C_{j\lambda} C_{j\sigma} \frac{\langle \hat{u}_{\mu\lambda}, (\hat{H}_{\text{core}}(i) - H_{ii}) \hat{u}_{\nu\sigma} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} \\ &= \frac{1}{2} \sum_{\mu} \sum_{\nu} C_{i\mu} C_{i\nu} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma} t_{(\mu\lambda, \nu\sigma)}^{\text{corr}}. \end{aligned} \quad (28)$$

Since

$$P_{\lambda\sigma} = 2 \sum_j C_{j\lambda} C_{j\sigma} \quad (29)$$

and

$$t_{(\mu\lambda, \nu\sigma)}^{\text{corr}} \stackrel{\text{def.}}{=} \frac{\langle \hat{u}_{\mu\lambda}, (\hat{H}_{\text{core}}(i) - H_{ii}) \hat{u}_{\nu\sigma} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} \quad (30)$$

Applying a similar treatment to the v_{ij}^{corr} , we obtain the following expression for the LCAOMO energy:

$$E_{\text{MO}} = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \left\{ H_{\mu\nu} + \frac{1}{4} \sum_{\lambda, \sigma} P_{\lambda\sigma} t_{(\mu\lambda, \nu\sigma)}^{\text{corr}} + \frac{1}{2} \sum_{\lambda, \sigma} P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - \frac{1}{2}(\mu\sigma | \lambda\nu) + \frac{1}{2}v_{(\mu\lambda, \nu\sigma)}^{\text{corr}}] \right\}. \quad (31)$$

Since the integrals $t_{(\mu\lambda, \nu\sigma)}^{\text{corr}}$ and $v_{(\mu\lambda, \nu\sigma)}^{\text{corr}}$ cannot be evaluated at the present time, expression (31) is so far purely formal. However it does illustrate the way in which electron correlation acts as a kinetic energy correction to the core Hamiltonian matrix, and as a potential energy correction to the electron repulsion integrals. It is to be compared to the usual LCAOMO electronic energy involving the neglect of electron correlation:

$$E = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \left\{ H_{\mu\nu} + \frac{1}{2} \sum_{\lambda, \sigma} P_{\lambda\sigma} [(\mu\nu | \lambda\sigma) - (\mu\sigma | \lambda\nu)] \right\}. \quad (32)$$

The splitting of the pair correlation energies into kinetic and potential parts is necessary in order to form a critique of semi-empirical parameter schemes (Sect. 6). However, the derivation could equally well have been carried out on the total pair correlation energies themselves, leading to an expression which is more convenient for actual calculations:

$$E_{\text{corr}} = \frac{1}{4} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} \varepsilon_{(\mu\nu, \lambda\sigma)}^{\text{corr}} \quad (31 \text{ A})$$

4. Pair Correlation Energy Approximation

In atomic calculations [1], values of the diagonal terms, $\varepsilon_{\mu\nu}^{\text{corr}} \equiv \varepsilon_{(\mu\nu, \mu\nu)}^{\text{corr}}$, lie between 0 and 1 eV. We may expect that the "cross-terms" $\varepsilon_{(\mu\lambda, \nu\sigma)}^{\text{corr}}$, $\mu \neq \lambda$ and $\lambda \neq \sigma$, are much less in magnitude than the diagonal terms, and hence take very small values. Let us neglect the "cross-terms" as a first measure towards the use of Eq. (31). Then we have:

$$t_{(\mu\lambda, \nu\sigma)}^{\text{corr}} = \delta_{\mu\nu} \delta_{\lambda\sigma} t_{\mu\lambda}^{\text{corr}}, \quad (33)$$

$$v_{(\mu\lambda, \nu\sigma)}^{\text{corr}} = \delta_{\mu\nu} \delta_{\lambda\sigma} v_{\mu\lambda}^{\text{corr}}, \quad (34)$$

where $t_{\mu\lambda}^{\text{corr}} \equiv t_{(\mu\lambda, \mu\lambda)}^{\text{corr}}$, $v_{\mu\lambda}^{\text{corr}} \equiv v_{(\mu\lambda, \mu\lambda)}^{\text{corr}}$ and δ is the Kronecker δ .

Under these assumptions,

$$E_{\text{MO}} = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \left\{ \left(H_{\mu\nu} + \frac{1}{4} \delta_{\mu\nu} \sum_{\lambda} P_{\lambda\lambda} t_{\mu\lambda}^{\text{corr}} \right) + \frac{1}{2} \sum_{\lambda, \sigma} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) + \frac{1}{2} \delta_{\mu\nu} \delta_{\lambda\sigma} v_{\mu\lambda}^{\text{corr}}] \right\}. \quad (35)$$

Note that the correlation correction now is non-zero only for diagonal elements $H_{\mu\mu}$ of the core Hamiltonian, and when Coulomb electron-repulsion integrals $(\mu\mu|\lambda\lambda)$ are present in the repulsion integral summation. The expression for E_{MO} is suitable for use in full overlap or in zero differential overlap all-valence-electron methods, further approximations to the electron repulsion integrals being made in the latter case. In either case the virial theorem may be introduced to give the final expression:

$$E_{\text{MO}} = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \left\{ H_{\mu\nu} - \frac{1}{4} \delta_{\mu\nu} \sum_{\lambda} P_{\lambda\lambda} \varepsilon_{\mu\lambda}^{\text{corr}} + \frac{1}{2} \sum_{\lambda, \sigma} P_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) + \delta_{\mu\nu} \delta_{\lambda\sigma} \varepsilon_{\mu\lambda}^{\text{corr}}] \right\}. \quad (36)$$

More simply, corresponding to Eq. (31 A), we have:

$$E_{\text{corr}} = \frac{1}{4} \sum_{\mu} \sum_{\nu} P_{\mu\mu} P_{\nu\nu} \varepsilon_{\mu\nu}^{\text{corr}}. \quad (36 \text{ A})$$

The $P_{\mu\nu}$, $H_{\mu\nu}$ and $(\mu\nu|\lambda\sigma)$ are determined by an ordinary LCAOMOSCF calculation, but the question of the values to be assigned to the pair correlation energies over atomic orbitals, $\varepsilon_{\mu\lambda}^{\text{corr}}$, in molecular calculations must now be considered.

5. Determination of Pair Correlation Energies for Molecular Calculations

One-centre pair correlation energies present less difficulty than two-centre correlation energies in practice. In the spirit of atoms-in-molecules approach [21], we may use the pair correlation energies already calculated for atoms as the one-

centre energies for molecules. The values listed in Table 1 are appropriate, although these may be replaced as better values become available [22].

For the time being a very simple approach to the calculation of two-centre pair correlation energies is taken. We make the series of assumptions, using *A* and *B* to represent different centres:

$$(i) \ (\epsilon_{\mu\nu}^{AB})^{\text{corr}} = \frac{1}{2}(\epsilon_{\mu\mu} + \epsilon_{\nu\nu}) \quad \text{at} \quad R_{AB} = 0, \quad (37)$$

$$\epsilon_{\mu\nu}^{\text{corr}} = 0 \quad \text{at} \quad R_{AB} = \infty; \quad (38)$$

(ii) in the bonding region, a direct proportionality to the amount of overlap of orbitals χ_μ and χ_ν applies.

$$\epsilon_{\mu\nu}^{\text{corr}} \propto S_{\mu\nu} \quad (39)$$

for $R_{AB} \approx R_e$, the equilibrium bond length.

(iii) Electron correlation is still active when there is no overlap ($S_{\mu\nu} = 0$) and manifests itself as the well-known London dispersion inter-molecular forces which are known to depend on the inverse sixth power of the internuclear distance [23], leading to the assumption:

$$\epsilon_{\mu\nu}^{\text{corr}} \propto R_{AB}^{-6}, \quad R_{AB} \gg R_e. \quad (40)$$

An expression of the form

$$\epsilon_{\mu\nu}^{\text{corr}} = \frac{\frac{1}{2}(\epsilon_{\mu\mu}^{\text{corr}} + \epsilon_{\nu\nu}^{\text{corr}})}{k_1 S_{\mu\nu}^{-1} + \frac{1}{2}k_2 (\epsilon_{\mu\mu}^{\text{corr}} + \epsilon_{\nu\nu}^{\text{corr}}) R_{AB}^6} \quad (41)$$

satisfies these assumptions. The only molecule in which pair correlation energies have been studied sufficiently to calibrate Eq. (41) is the hydrogen molecule. Thus the constant k_2 is found from the known van der Waals' interaction energy in hydrogen when $S_{\mu\nu} = 0$, and then k_1 is determined from the known value of the two-centre correlation energy at the equilibrium bond length. With the data:

$$\epsilon_{1s}^{\text{corr}} = 1.1430 \text{ eV for helium } (R=0) \text{ [24],}$$

$$(\epsilon_{1s,1s}^{AB})^{\text{corr}} = 1.1122 \text{ eV for H}_2, R_e = 0.74084 \text{ \AA}$$

and $S_{1s,1s}^{AB} = 0.675997$, calculated in this work using the orbital exponents $S_{1s} = 1.197$ [25], we use also the quantum mechanical proportionality constant for London dispersion forces ϕ_{AB}^{disp} [23]:

$$\begin{aligned} \phi_{AB}^{\text{disp}} &= C/R_{AB}^6 \\ &= -6.50 e^2 a_0^5/R_{AB}^6 \end{aligned} \quad (42)$$

then

$$\begin{aligned} k_2 &= -1/C \\ &= -0.257505 (\text{\AA})^{-6} (\text{eV})^{-1} \end{aligned}$$

and with this k_2 value, $k_1 = 0.734424$.

Finally invariance of the two-centre correlation formula to rotations of local axes is ensured by taking average valence shell overlap integrals between orbitals of the same type on the participating centres (eq. S_{sp}^-, S_{pp}^- , etc.):

$$S_{\mu\nu}^- = \sum_{\mu}^A \sum_{\nu}^B \frac{S_{\mu\nu}}{n_{\mu}^A n_{\nu}^B} \quad (43)$$

the sums being over all orbitals of the same n and l quantum numbers on each centre, and n_μ^A, n_ν^B being the respective numbers of such orbitals.

Thus two-centre pair correlation energies in the general case are given by:

$$\varepsilon_{\mu\nu}^{\text{corr}} = \frac{\frac{1}{2}(\varepsilon_{\mu\mu}^{\text{corr}} + \varepsilon_{\nu\nu}^{\text{corr}})}{0.7344 S_{\mu\nu}^{-1} - 0.2575 \cdot \frac{1}{2}(\varepsilon_{\mu\mu}^{\text{corr}} + \varepsilon_{\nu\nu}^{\text{corr}}) R_{AB}^6}. \quad (44)$$

Knowing the atomic monocentric pair correlation energies from the Table, correlation corrections in the molecular orbital energy, Eq. (35), are readily included in this approximate way.

Eq. (44) is rotationally invariant only for values of monocentric pair correlation energies that maintain the relationships of those in the Table, e.g., all $\varepsilon_{\text{corr}}(2p^2)$ on the one atom are taken to be the same, etc.

6. Relation to Semi-Empirical Parameter Schemes

The electron correlation derivation suggests a number of relationships important in understanding semi-empirical parameter schemes. In such schemes, elements of the core Hamiltonian together with Coulomb and exchange repulsion integrals are estimated in a semi-empirical manner, and the remainder of the energy is either calculated from these parameters (full overlap methods) or neglected (differential overlap methods). Let us therefore consider only that portion of the energy containing the semi-empirical parameters (denoted by the subscript "se"):

$$E_{\text{se}} = \sum_{\mu} P_{\mu\mu} \left\{ H_{\mu\mu}^{\text{se}} + \frac{1}{2} P_{\mu\mu} (\mu\mu|\mu\mu)_{\text{sc}} + \sum_{\lambda \neq \mu} \frac{1}{2} P_{\lambda\lambda} [(\mu\mu|\lambda\lambda)_{\text{se}} - \frac{1}{2}(\mu\lambda|\lambda\mu)_{\text{sc}}] \right\} \\ + \sum_{\mu} \sum_{\nu \neq \mu} P_{\mu\nu} \left\{ H_{\mu\nu}^{\text{se}} + \frac{1}{2} P_{\mu\nu} [\frac{3}{2}(\mu\nu|\nu\mu)_{\text{sc}} - \frac{1}{2}(\mu\mu|\nu\nu)_{\text{se}}] \right\} \quad (45)$$

From Eq. (35), this same portion of the energy including correlation is given by:

$$E^1 = \sum_{\mu} P_{\mu\mu} \left\{ \left[H_{\mu\mu} - \frac{1}{4} \sum_{\lambda} P_{\lambda\lambda} \varepsilon_{\mu\lambda}^{\text{corr}} \right] + \frac{1}{4} P_{\mu\mu} [(\mu\mu|\mu\mu) + 2\varepsilon_{\mu\mu}^{\text{corr}}] \right. \\ \left. + \sum_{\lambda \neq \mu} \frac{1}{2} P_{\lambda\lambda} [(\mu\mu|\lambda\lambda) - \frac{1}{2}(\mu\lambda|\lambda\mu) + \varepsilon_{\mu\lambda}^{\text{corr}}] \right\} \\ + \sum_{\mu} \sum_{\nu \neq \mu} P_{\mu\nu} \left\{ H_{\mu\nu} + \frac{1}{2} P_{\mu\nu} [\frac{3}{2}(\mu\nu|\nu\mu) - \frac{1}{2}(\mu\mu|\nu\nu) + \varepsilon_{\mu\nu}^{\text{corr}}] \right\}. \quad (46)$$

As observed before, this is the only part of the energy in which correlation corrections need be made.

Experimental atomic valence state ionization potentials are normally used in the choice of $H_{\mu\mu}^{\text{se}}$. If χ_{μ} is an orbital on centre A, then:

$$H_{\mu\mu}^{\text{se}} = -I_{\mu} + \sum_{B \neq A} X_B \langle \mu | \hat{V}_B | \mu \rangle \quad (47)$$

where I_{μ} is the appropriate valence state ionization potential, X_B the core charge on atom B, and $\langle \mu | \hat{V}_B | \mu \rangle$ the nuclear attraction integral for an electron in orbital χ_{μ} and unit positive charge on atom B. Theoretically I_{μ} contains the kinetic energy integral and the nuclear attraction integral $X_A \langle \mu | \hat{V}_A | \mu \rangle$. We may suppose that it also contains the one-centre correlation correction since I_{μ} is an observed atomic

quantity: i.e.

$$I_{\mu} = \langle \mu | -\frac{1}{2} \hat{V}^2 | \mu \rangle + X_A \langle \mu | \hat{V}_A | \mu \rangle - \frac{1}{4} \sum_{\nu}^A n_{\nu} \epsilon_{\mu\nu}^{\text{corr}}. \quad (48)$$

Here n_{ν} is the atomic occupation number of orbital χ_{ν} in the valence state atom. The corresponding part of the correlation-corrected molecular core Hamiltonian is:

$$\langle \mu | -\frac{1}{2} \hat{V}^2 | \mu \rangle + X_A \langle \mu | \hat{V}_A | \mu \rangle - \frac{1}{4} \sum_{\nu} P_{\nu\nu} \epsilon_{\mu\nu}^{\text{corr}}. \quad (49)$$

Thus the use of a semi-empirical core Hamiltonian involves:

(i) The assumption that $n_{\nu} \approx P_{\nu\nu}$, i.e. orbital occupations remain similar in free atom and molecule.

(ii) The neglect of two-centre kinetic energy correlation corrections

$$\sum_{B \neq A} \sum_{\lambda}^B P_{\lambda\lambda} \epsilon_{\mu\lambda}^{\text{corr}},$$

a quantity likely to increase as larger molecules are considered.

The semi-empirical electron repulsion integral $(\mu\mu|\mu\mu)_{\text{se}}$ is replaced by $[(\mu\mu|\mu\mu) + 2\epsilon_{\mu\mu}^{\text{corr}}]$ in the more exact expression. Whereas the same $(\mu\mu|\lambda\lambda)_{\text{se}}$, $\mu \neq \lambda$, is used in both diagonal and off-diagonal parts of E_{se} , expression (46) shows that different values should be used,

$$(\mu\mu|\lambda\lambda) + \epsilon_{\mu\lambda}^{\text{corr}} \quad \text{in the diagonal part,}$$

$$(\mu\mu|\lambda\lambda) - 2\epsilon_{\mu\lambda}^{\text{corr}} \quad \text{in the off-diagonal part.}$$

If these corrections are made to the Coulomb repulsion integrals, no adjustment of exchange repulsion integrals for electron correlation is required. Therefore either non-empirical exchange repulsion integrals may be used directly in semi-empirical schemes, or these integrals may be found from empirical Slater-Condon parameters as suggested in the previous paper [5].

Note that the proper way to allow for correlation effects, when the correlation part of the wave function is not specifically found, is to apply the correlation correction, via Eq. (36), to calculate the total energy *after* the form of the MO's, Eq. (20), has been determined by solution of the Roothaan SCF equation. However the semi-empirical parameter schemes, *if they are assumed to include an energy allowance for correlation*, imply an erroneous discussion of $(\mu\mu|\mu\mu)_{\text{se}}$ and $(\mu\mu|\lambda\lambda)_{\text{se}}$, prior to the computation of the Hartree-Fock eigenvectors.

The derivation of this paper seems to have produced a very simple yet valuable method of making an energy correction for electron correlation. The method may be readily used in conjunction with accurate molecular Hartree-Fock (LCAO) calculations as well as with approximate MO theory. Its practical promise has been demonstrated elsewhere [27]. An investigation of the effects of electron correlation on molecular wave functions and electron densities is presently under way.

Acknowledgements. One of us (KRR) would like to thank Dr. Önder Pamuk for a discussion of the material presented here. Dr. Pamuk has independently derived an expression similar to (35) by a different route.

References

1. Sinanoğlu, O.: *Advances chem. Physics* **6**, 315 (1964).
2. Löwdin, P. O.: *Advances chem. Physics* **2**, 207 (1959).
3. Nesbet, R. K.: *Advances chem. Physics* **9**, 321 (1965).
4. Brown, R. D., Roby, K. R.: *Theoret. chim. Acta (Berl.)* **16**, 175 (1970) (Part I).
5. — — *Theoret. chim. Acta (Berl.)* **16**, 194 (1970) (Part II).
6. — — *Theoret. chim. Acta (Berl.)* **16**, 278 (1970) (Part III).
7. Nesbet, R. K.: *Physic. Rev.* **109**, 1632 (1958).
8. Allen, L. C., Clementi, E., Gladney, H. M.: *Rev. mod. Physics* **35**, 465 (1963).
9. Ruedenberg, K.: *Rev. mod. Physics* **34**, 326 (1962).
10. Salem, L.: *Molecular orbital theory for conjugated systems*. New York: W. A. Benjamin Inc. 1966.
11. McKoy, V., Sinanoğlu, O.: *J. chem. Physics* **41**, 2689 (1964).
12. — — *Modern quantum chemistry, Part II*, ed. by O. Sinanoğlu. New York and London: Academic Press 1965.
13. Clementi, E.: *J. chem. Physics* **38**, 2248 (1963).
14. — *J. chem. Physics* **39**, 175 (1963).
15. — *J. chem. Physics* **42**, 2785 (1965).
16. Hollister, C., Sinanoğlu, O.: *J. Amer. chem. Soc.* **88**, 13 (1966).
17. Parr, R. G.: In: *Molecular orbitals in chemistry, physics and biology*, ed. by P. O. Löwdin and B. Pullman. New York and London: Academic Press 1964.
18. Kutzelnigg, W.: *Theoret. chim. Acta (Berl.)* **1**, 343 (1963).
19. Sinanoğlu, O.: *Rev. mod. Physics* **35**, 517 (1963).
20. Roothaan, C. C. J.: *Rev. mod. Physics* **23**, 69 (1951).
21. Moffitt, W.: *Proc. Roy. Soc. (London) A* **210**, 245 (1951).
22. Sinanoğlu, O., Öksüz, I.: To be published.
23. Hirschfelder, J. O., Curtiss, C. F., Bird, R. B.: *Molecular theory of gases and liquids*. New York: John Wiley and Sons 1954.
24. Roothaan, C. C. J., Weiss, A.: *Rev. mod. Physics* **32**, 194 (1960).
25. Parr, R. G.: *The quantum theory of molecular electronic structure*. New York: W. A. Benjamin 1963.
26. Tuan, D. F., Sinanoğlu, O.: *J. chem. Physics* **41**, 2677 (1964).
27. Roby, K. R., Sinanoğlu, O.: *Int. J. quant. Chem., Eyring Symposium Issue* (to be published).

Professor R. D. Brown
Department of Chemistry
Monash University
Clayton, Victoria, Australia 3168