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On the Importance of Correlation Effects for the Parameters of Semi-Empirical Molecular Orbital Calculations

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The one- and two-center coulomb repulsion parameters of semi-empirical molecular orbital calculations are commonly assumed to incorporate some correlation effects. It is shown that the horizontal correlation energy in a two-electron diatomic molecule can indeed be combined with the one- and two-center coulomb integrals to yield "correlated parameters". However, the theoretical expressions for these parameters show a dependence on the internuclear separation which is strongly at variance with the common assumptions. The results indicate that a theoretical elucidation of the semi-empirical parameters is not likely to be found by consideration of correlation effects in a single electronic state.

I.a. wird angenommen, daß die Parameter semiempirischer MO-Rechnungen Korrelationseffekte miterfassen. Für H_2 wird gezeigt, daß die horizontale Korrelation sich tatsächlich durch Verwendung „korrelierter Parameter" beschreiben läßt. Jedoch unterscheidet sich die theoretische Abhängigkeit dieser Parameter vom Kernabstand von der üblicherweise angenommenen. Es ist nicht möglich, die Parameter semiempirischer MO-Methoden durch Untersuchung der Korrelation nur eines Zustandes theoretisch zu errechnen.

Les paramètres coulombiens de répulsion à un et deux centres des calculs semi-empiriques d'orbitales moléculaires sont habituellement supposés tenir compte de certains effets de corrélation. On montre que l'énergie de corrélation horizontale dans une molécule diatomique à deux électrons peut cependant être combinée avec les intégrales de coulomb à un et deux centres pour fournir des "paramètres corrélés". Mais les expressions théoriques pour ces paramètres montrent une variation avec la distance internucléaire très différente de celle supposée habituellement. Ces résultats montrent qu'un éclaircissement théorique des paramètres semi-empiriques ne sera sans doute pas obtenu par la considération des effets de corrélation dans un état électronique unique.

Introduction

In semi-empirical organic or inorganic molecular orbital calculations the total energy of the peel electrons [1] is expressed in terms of certain one- and two-center integrals. (For reviews of these semi-empirical approaches see [2, 3]). It is now an inherent assumption in all semi-empirical calculations that the correct energy expression for the electronic system in question emerges in a form essentially similar to the result of a simple molecular orbital calculation. In particular, it is assumed that the coefficients in front of the above mentioned integrals can be retained from the simpler treatment, and that major parts of the errors can be corrected by assigning appropiate values to the integrals, which are consequently called parameters. The success of such schemes, the PARISER, PARR and POPLE method [2] or the WOLFSBERG, HELMHOLZ method [3] and variations thereof, certainly lends substantial credibility to this assumption. However, the lack of sufficiently accurate wavefunctions for even medium size molecules has apparently prevented any *a priori* demonstration of its validity.

FISCHER-HJALMARS [4, 5] and SINANOĞLU and ORLOFF [6] have in recent discussions ascribed the major part of the deviation between the semi- and non-empirical values of the parameters to correlation effects, i.e. errors inherent in the independent particle scheme underlying any molecular orbital approach. DEWAR [7] has likewise in the split-orbital method based his arguments on correlation considerations. Inaccuracies associated with the core-peel separation [1], which is ordinarily invoked, and deficiencies of the Slater atomic orbitals as basis for molecular calculations are both assumed to play a minor role.

The many-electron-theory put forward by SINANOĞLU [8] showed that the largest part of the correlation energy of a closed shell electronic system can be written as a sum over pair-correlation terms. On this basis SINANOĞLU and ORLOFF argued that these pair-correlation terms can be split into parts which subsequently can be combined with the one- and two-center coulomb repulsion integrals of the molecular orbital scheme to yield the parameters of the semi-empirical methods. However, they did not actually perform this reduction of the molecular correlation energy. In the subsequent discussion these authors, in line with the work of FISCHER-HJALMARS [4, 5], used atomic correlation data to obtain the one-center parameters, and turned to valence-bond considerations to estimate the two-center parameters. The choice of the valence-bond wavefunctions for the discussion of the two-center parameters was made explicitly to circumvent the well-known problem of the inaccuracy of a molecular orbital wave function for large internuclear separations [9]. However, since the parameters are actually employed in a molecular orbital scheme it seems pertinent to investigate a little closer what the effects of correlation are in this case.

We shall in the present communication consider the effect of horizontal correlation in the ground state of a diatomic two-electron molecule, and show that a major part of this correlation can indeed be incorporated in parameters corresponding to the one- and two-center coulomb repulsion integrals. However, the derived theoretical expressions for these parameters do not show the behaviour commonly assumed in the Pariser-Parr-Pople-type calculations. This is discussed further in the concluding section.

Effect of Horizontal Correlation

In a diatomic molecule the correlation energy can conveniently be divided into three parts corresponding to the three cylindrical coordinates: in-out correlation, angular correlation and horizontal (or left-right) correlation [10]. The in-out and angular parts have corresponding counterparts in atomic systems [11], whereas the horizontal correlation is peculiar to the molecular electronic system. The following discussion is restricted to the horizontal correlation energy. Firstly because this contribution is known to account for more than 50 percent of the total correlation in the hydrogen molecule (at equilibrium distance) [10], and secondly because the relative importance of angular and in-out correlation will depend strongly on the details of the molecular orbitals in each particular case.

Consider a two-electron homonuclear diatomic molecule. The two lowest molecular orbitals can be written as linear combinations of atomic orbitals χ_1 and χ_2 associated with nuclei 1 and 2:

$$\theta_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2),$$

$$\theta_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2),$$

where the zero-differential-overlap (z.d.o.) approximation

$$\chi_p(1)\,\chi_q(1) = \delta_{pq}\,\chi_p(1)\,\chi_p(1) \tag{1}$$

is invoked in order to conform with common usage in semiempirical calculations [2]. This approximation can be interpreted as the use of LØWDIN orthogonalized orbitals followed by consistent application of the Mulliken approximation for all two-center overlap distributions [12]. The ground configuration of this molecule is the determinantal wavefunction

$$\Psi_0 = |\,\theta_1\,\bar{\theta}_1\,|\,.$$

The two-electron hamiltonian for this system can in the fixed nuclei approximation be written:

$$H = H_c(1) + H_c(2) + \frac{e^2}{r_{12}} \tag{2}$$

where the core-hamiltonian $H_c(i)$ contains the kinetic energy and the attractive potential from the nuclei for the i'th electron. Using the hamiltonian in the form (2) and applying the z.d.o. approximation (1) the energy of Ψ_0 can by standard methods be obtained as

$$E(\Psi_0) = \alpha_1 + \alpha_2 + 2\beta_{12} + \tfrac{1}{2}(\gamma_{11} + \gamma_{12})\,, \tag{3}$$

where

$$\alpha_p = \int \chi_p\,H_c\,\chi_p\,d\tau\,, \qquad \beta_{pq} = \int \chi_p\,H_c\,\chi_q\,d\tau\,,$$

$$\gamma_{pq} = \int\!\!\int \chi_p(1)\,\chi_q(2)\,\frac{e^2}{r_{12}}\,\chi_p(1)\,\chi_q(2)\,d\tau_1\,d\tau_2\,.$$

The predominant part of the horizontal correlation energy can now be taken into account by allowing the ground configuration Ψ_0 to interact with the doubly excited configuration [9, 10]

$$\Psi_2 = |\,\theta_2\,\bar{\theta}_2\,|$$

with energy

$$E(\Psi_2) = \alpha_1 + \alpha_2 - 2\beta_{12} + \tfrac{1}{2}(\gamma_{11} + \gamma_{12})\,. \tag{4}$$

The "horizontally correlated" ground state function is accordingly

$$\Phi_0 = \sqrt{1-\lambda^2}\,\Psi_0 + \lambda\,\Psi_2\,, \tag{5}$$

where the mixing coefficient, λ, to a good approximation can be obtained from perturbation theory if needed. What is most important for the present discussion is that λ is inherently negative for the present choice of phases. This follows from the first order expression

$$\lambda \simeq \frac{H_{02}}{E(\Psi_0) - E(\Psi_2)}\,; \tag{6}$$

the denominator is always negative (or zero) whereas the numerator

$$H_{02} = \int \Psi_0 \, H \, \Psi_2 d\tau = \tfrac{1}{2}(\gamma_{11} - \gamma_{12}) \tag{7}$$

is positive for non-vanishing internuclear separation. Furthermore, λ is a function of the internuclear separation decreasing asymptotically towards $-1/\sqrt{2}$ as the separation goes to infinity [9]. This is seen by observing that Ψ_0 and Ψ_2 in this case become degenerate, since both of the two-center integrals β_{12} and γ_{12} vanish. Combining Eqs. (3), (4), (5) and (7) we obtain the energy of Φ_0:

$$\begin{aligned} E(\Phi_0) &= (1 - \lambda^2)\, E(\Psi_0) + 2\lambda \sqrt{1-\lambda^2}\, H_{02} + \lambda^2\, E(\Psi_2) \\ &= \alpha_1 + \alpha_2 + 2(1 - 2\,\lambda^2)\, \beta_{12} + \\ &+ \tfrac{1}{2}(1 + 2\lambda \sqrt{1-\lambda^2})\, \gamma_{11} + \tfrac{1}{2}(1 - 2\lambda \sqrt{1-\lambda^2})\, \gamma_{12} \end{aligned}$$

or

$$E(\Phi_0) = \alpha_1 + \alpha_2 + 2\beta'_{12} + \tfrac{1}{2}(\gamma'_{11} + \gamma'_{12}) \tag{8}$$

where the primed integrals are defined as

$$\beta'_{12} = (1 - 2\,\lambda^2)\, \beta_{12}\,, \tag{9a}$$

$$\gamma'_{11} = (1 + 2\,\lambda \sqrt{1-\lambda^2})\, \gamma_{11}\,, \tag{9b}$$

$$\gamma'_{12} = (1 - 2\,\lambda \sqrt{1-\lambda^2})\, \gamma_{12}\,. \tag{9c}$$

Hence by this straight-forward configuration interaction calculation we have arrived at a horizontally correlated energy expression (8) which is formally identical to the simpler expression (3), provided the proper integral values (9) are inserted. Eq. (9) therefore represent a set of theoretical expressions for the one- and two-center parameters. The derivation has then primarily shown that for this simple system, which in a sense is a prototype for alternant hydrocarbons, it is certainly possible to account for a large fraction of the correlation energy of the ground state by suitable changes of the values of exactly those integrals which are considered parameters in the semi-empirical approaches.

Of the three parameters (9) the *core-integral* β'_{12} is seen to be the least sensitive to horizontal correlation, since the correction is of second order in the mixing coefficient λ. This is in good agreement with the fact that non-empirically computed β-integrals are known to be quite close to the semiempirical values.

However, the two *γ-parameters* (9b) and (9c) behave entirely differently from the generally accepted coulomb-repulsion parameters [2]. It was noted previously that λ is negative and decreases asymptotically towards $-1/\sqrt{2}$ as the internuclear distance goes to infinity. This implies that γ'_{11} is always smaller than γ_{11}, as is usually assumed, however, it is strongly dependent on the interatomic distance and is actually vanishing for large separation. γ'_{11} is hence not a local quantity (i.e. a quantity depending solely on the nature of atom 1). This is clearly at variance with the idea of using atomic correlation data to estimate this parameter.

The two-center coulomb repulsion parameter γ'_{12} is on the other hand always larger than the non-empirical value for γ_{12}, the distance dependence here being such that γ'_{12} approaches twice the value of γ_{12} for large separations. This is in noteworthy contrast to the general assumption that the semi-empirical value of this parameter approaches the non-empirical for large interatomic distances. The λ dependence of the two coulomb repulsion parameters has the consequence that

γ'_{12} is larger than γ'_{11} for interatomic distances larger than a certain value, which in hydrogen turns out to be less than the equilibrium separation.

Discussion

The behaviour of the parameters (9b) and (9c) is easily explained on physical ground. The coefficient of the one-center repulsion integral, γ_{11}, indicates the amount of ionic character in the wavefunction, whereas the coefficient of γ_{12} shows the amount of covalent character. In a simple molecular orbital wavefunction the two structures are known to be equally represented, as witnessed by the mutual factor of $\frac{1}{2}$ for the two integrals in Eq. (3) [*13*]. What is done in Eqs. (9) is really to assign different weights to the two integrals according to the changes in the relative amounts of ionic and covalent structures which result from the configuration interaction (5) [*9*]. At large internuclear separations the wavefunction becomes entirely covalent, and the one-center repulsion must consequently disappear, as indeed it does. The equations therefore reflect some well-established features of elementary valence chemistry. It may be added that this behaviour of the coulomb repulsion parameters will obtain quite generally whenever the separated atom (or separated fragment) limit for the principal molecular orbital configuration for a particular state corresponds to nonstationary states of the fragments. This in turn is the expected situation whenever the proper dissociation limit contains fragments with non-closed shells*.

It must be emphasized that the results of this discussion are not to be interpreted to mean that the relations (9) should be used to evaluate the parameters for a Pariser-Parr-Pople-type calculation. However, they do indicate that a theoretical justification of the properties of the semi-empirical parameters is not likely to be found by considerations of correlation effects in a single electronic state. This conclusion is in agreement with the actual experimental determination of these parameters which are obtained from spectroscopic data involving a number of different states, since it can be expected that the correlation energies of different electronic states of a molecule will differ significantly. This expectation is supported by the results of the work of CRAIG [*15*] and some recent work by CRAIG and BERRY [*16*] which show that the excited states of benzene exhibit large differences in ionic character and hence in horizontal correlation. CLEMENTI [*14*] has in a study of atoms similarly found that different states, even states arising from the same configuration, have correlation energies which differ by amounts that are non-trivial compared to the splittings of the states.

In concluding we wish to point out one corollary of this conclusion, namely that a theoretical estimate of the form of the interpolation to use for two-center repulsion integrals according to this discussion requires explicit consideration of all the pertinent electronic states.

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