A Note on Electron Correlation in the Hydrogen Molecule*

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With 2 Figures

A few years ago *Coulson* and *Neilson*[1] discussed electron correlation in the helium atom. This correlation was measured by the mean value $\langle r_{12}^{-1} \rangle$ of the inverse distance between the two electrons. Different approximate wave functions give different values of $\langle r_{12}^{-1} \rangle$; one may say that if this quantity is large there is less correlation (smaller mean separation) that if it is small. These authors drew attention to a curious empirical relationship, that if ΔE denoted the energy difference between the approximate and true energies, then ΔE varied linearly with $\langle r_{12}^{-1} \rangle$, and was of the form

$$\Delta E = \text{const.} + c \langle r_{12}^{-1} \rangle \tag{1}$$

where c had the numerical value $c = \dfrac{1}{2}$. The positive sign of c implied that increasing electron correlation led to a lowering of the energy. Subsequently *Robinson*[2] and *Cohen*[3] tried to establish conditions under which this empirical relationship could be shown to hold theoretically. However, very recently, *Jankowski*[4] has shown that the simple relation (1)

[1] *C. A. Coulson* and *A. H. Neilson*, Proc. Phys. Soc. **78**, 831 (1961).

[2] *P. D. Robinson*, Proc. Phys. Soc. **82**, 659 (1963).

[3] *M. Cohen*, J. Molec. Spectroscopy **17**, 1 (1965).

[4] *K. Jankowski*, Bull. Acad. Polonaise des Sciences, ser. math. astr. and phys. **14**, 163 (1966).

does not always hold, and that it is possible to devise a family of reasonably accurate wave functions for which the energy varies with $\langle r_{12}^{-1} \rangle$ in the opposite way to that found for the set of approximate functions considered by *Coulson* and *Neilson*.

It is the object of the present note to show, by considerations of the ground state of H_2, that *Jankowski*'s finding applies to molecules as well as to atoms. The analysis itself is very straightforward, and so there is no need to describe the calculations in detail.

Let us consider the two forms (2) and (3) for approximate wave functions for H_2:

$$\psi = N \{\psi_{\text{cov}} + k\,\psi_{\text{ion}}\},\tag{2}$$

where

$$\psi_{\text{cov}} = \varphi_a(1)\,\varphi_b(2) + \varphi_b(1)\,\varphi_a(2)$$

$$\psi_{\text{ion}} = \varphi_a(1)\,\varphi_a(2) + \varphi_b(1)\,\varphi_b(2),$$

and

$$\psi = N' \{(\sigma\,1s)^2 - \lambda\,(\sigma^*\,1s)^2\},\tag{3}$$

where

$$(\sigma\,1s) = \varphi_a + \varphi_b$$

$$(\sigma^*\,1s) = \varphi_a - \varphi_b$$

and φ_a, φ_b are normalized 1 s-atomic orbitals around the two nuclei A, B, of the form

$$\varphi_a = \sqrt{\frac{\zeta}{\pi}}\,exp\,(-\zeta\,r_a).\tag{4}$$

N and N' are normalizing factors of no great interest to us. Wave function (2) represents standard covalent-ionic resonance, and (3) represents standard configuration-interaction in the molecular-orbital theory. *Coulson* and *Fischer*[5] showed that (2) and (3) are identical if

$$k = (1 - \lambda)/(1 + \lambda)\tag{5}$$

We may therefore consider a family of trial functions in terms either of the parameters k or of λ. We have evaluated $\langle r_{12}^{-1} \rangle$ as well as the total energy E, for this family as a function of k, [see e.g. reference[6]], in each case minimizing E by varying the screening constant ζ. In these calculations the interatomic distance R was always taken to have the equilibrium value 1.40 a_0. The table below shows the connection between k and λ and also the appropriate values of ζ obtained in this way.

[5] *C. A. Coulson* and *I. Fischer*, Phil. Mag. **40**, 386 (1949).

[6] (a) *M. P. Barnett, F. W. Birss*, and *C. A. Coulson*, Molec. Phys. **1**, 44 (1958). (b) *J. C. Slater*, "Quantum Theory of Molecules and Solids", Vol. 1, McGraw-Hill Book Company, New York, chap. 3 (1963).

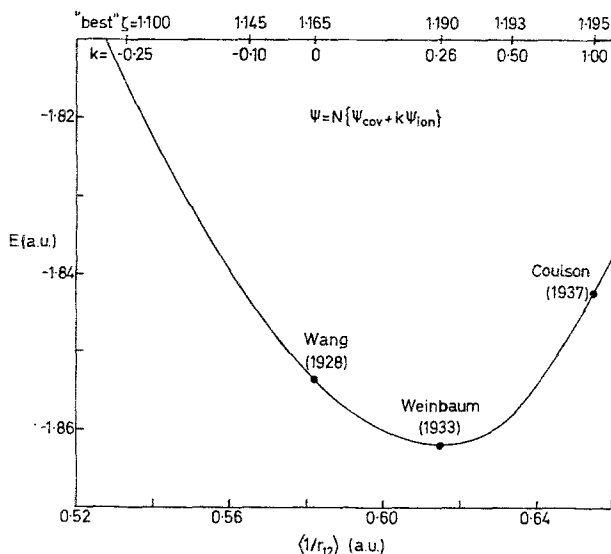| k	$=$	0	0.26	1.0	∞
λ	$=$	1	0.59	0	—1
description		pure covalent[7]	"best"	pure molecular orbital[9]	pure ionic
		over-correlated	function[8]	under-correlated	under-correlated
ζ	$=$	1.165	1.193	1.195	1.065

Fig. 1. Total electronic energy E as function of $\langle r_{12}^{-1} \rangle$ for the family of wave functions (2). Calculations were made for the five values of k marked along the abscissa. Also shown are the appropriate values of the orbital exponent ζ which minimize E. All quantities are in atomic units

In Fig. 1 we show the variation of E as a function of $\langle r_{12}^{-1} \rangle$ for this family. It is immediately obvious that there is no kind of linear variation of E with $\langle r_{12}^{-1} \rangle$ and that we have a situation similar to that found for He by *Jankowski*[4]; as k varies from 0 to ∞ (or λ varies from $+ 1$ to $— 1$) we change from an over-correlated wave function to an under-correlated one. It follows that in this family of wave functions, it is not correct to say (as is often said in general terms) that if we allow for greater electron correlation we shall lower the energy. Fig. 1 shows that, if we approach the "best" wave function from the pure molecular-orbital form, this relation holds, but if the same wave function is approached from the pure covalent form, precisely the opposite holds.

[7] S. C. *Wang*, Phys. Rev. **31**, 579 (1928).

[8] S. *Weinbaum*, J. Chem. Phys. **1**, 593 (1933).

[9] C. A. *Coulson*, Trans. Faraday Soc. **33**, 1479 (1937).

It is interesting to analyse this situation a little more closely. The total energy E is the sum of several terms:

$$E = \langle T \rangle + \langle V_{en} \rangle + \langle r_{12}^{-1} \rangle + 1/R \qquad (6)$$

where $\langle T \rangle$ is the kinetic energy (strictly, the quantum-mechanical mean kinetic energy) and $\langle V_{en} \rangle$ is the electron-nuclear potential energy of
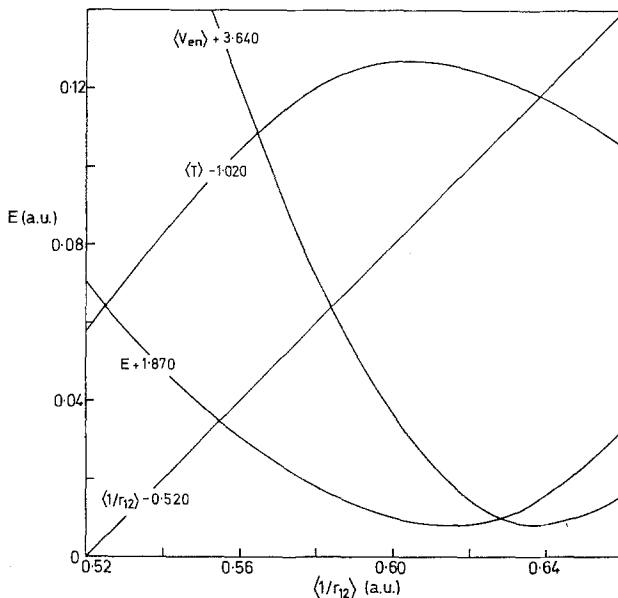

Fig. 2. Same as Fig. 1 but here the variation of the kinetic energy $\langle T \rangle$, and the nucleus-electron potential energy $\langle V_{en} \rangle$ are also shown. In order to facilitate comparisons, different zeros are chosen for the different quantities

attraction. In our case the last term of (6) is constant; the variations of the other terms and also of E are shown in fig. 2 as a function of $\langle r_{12}^{-1} \rangle$. In order to facilitate comparisons of their rates of change, different zeros are chosen for all four quantities in fig. 2, but the same scale is used for them all.

It is immediately obvious from (6) that there will be a linear relation between E and $\langle r_{12}^{-1} \rangle$ if $\langle T \rangle + \langle V_{en} \rangle$ varies linearly with $\langle r_{12}^{-1} \rangle$. One condition for this[10] is that the virial theorem shall be satisfied. In our case this is ensured by use of the variation method for the scale factor ζ. A second condition[11] is that we shall be sufficiently near the *Hartree—Fock* (i.e. best possible molecular-orbital) wave function that the first-order cor-

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[10] *K. Jankowski*, Acta Phys. Polon. **30**, 109 (1966).
[11] *M. Cohen* and *A. Dalgarno*, Proc. Phys. Soc. **77**, 748 (1963).

rections to the expectation values of the one-electron operators for $\langle T \rangle$ and $\langle V_{\mathrm{en}} \rangle$ shall vanish. Fig. 2 does indeed show that in the region ($k > 0.26$) where E and $\langle r_{12}^{-1} \rangle$ vary in the same sense, $\langle T \rangle$ and $\langle V_{\mathrm{en}} \rangle$ are nearly constant; but in the region $k < 0.26$ where E and $\langle r_{12}^{-1} \rangle$ vary in the opposite sense, neither $\langle T \rangle$ nor $\langle V_{\mathrm{en}} \rangle$ nor their sum is even approximately constant.

There is an interesting and simple physical interpretation of the results of this note. If we start with the pure m. o. function ($k = 1.0$) and decrease k, we introduce some electron correlation. This serves to reduce $\langle r_{12}^{-1} \rangle$ by keeping the electrons further apart: and at first it can be achieved without too much other restriction on the two electrons. However, when we further decrease k, and so introduce more correlation, there comes a stage at which, as we keep the electrons far apart from each other, we force them farther from the nuclei. When this occurs $\langle V_{\mathrm{en}} \rangle$ increases. At this stage the total energy begins to rise, and not fall. Too much correlation is as bad for the energy as too little.

It may be added that a curve similar in general appearance to that of Fig. 1 is also found if we make all our calculations with unscaled atomic orbitals for which $\zeta = 1$. These functions, however, do not satisfy the virial theorem, and we should not therefore expect (1) to apply.