

## On the Coupling between Electronic and Nuclear Motion and Van der Waals' Interaction between Helium Atoms

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Figure 2 is a revised chart<sup>1,8</sup> which shows at a glance the systematic relation of electronegativity to the periodic system of the elements. Within a given period, electronegativity increases with increase of atomic number in an orderly sequence except for the *B* subgroup elements of periods IV, V, and VI. For the latter, the electronegativities of elements of the first group are actually higher than those of the center group. This interruption of the orderly sequence can be attributed to the incomplete screening by subvalence electrons which in these elements have energy comparable to that of the valence electrons.

The electronegativity values which we list in Table I should be regarded as mean values or probable values for the most common form of bonding of the given element. For illustration, evidence indicates<sup>11</sup> that  $\alpha$  values for carbon range from about 2.3 in  $\text{H}_3\text{C}-$  to about 2.8 in  $\text{N}\equiv\text{C}-$ . The value 2.5 selected by Pauling is probably the most representative value. Similar variations are to be expected for certain other elements. Nevertheless, it is evident from the comparisons in Table I alone, that electronegativity is a highly useful concept, one which allows the correlation of a wide variety of chemical and physical phenomena.

## On the Coupling between Electronic and Nuclear Motion and Van der Waals' Interaction between Helium Atoms

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The analytical expression for the potential due to the coupling between the electronic and the nuclear motion for two normal helium atoms has been obtained for a wave function of the form of that of P. Rosen. This coupling interaction is a repulsive potential and is to be added to the usual "valence" and Van der Waals' potential obtained in the static-nuclei approximation. This coupling interaction, being inversely proportional to the reduced mass of the two interacting atoms, contributes to a weaker binding between two  $\text{He}^3$  atoms than between two  $\text{He}^4$  atoms.

IN a recent note,<sup>1</sup> it has been shown that for light atoms, the effect of the coupling between the electronic and the nuclear motion on the potential between a pair of atoms is not negligible compared with the Van der Waals' interaction calculated in the usual static-nuclei approximation, in the range of nuclear separations in which the latter is appreciable. In that note, calculations have been carried out for the lowest states of  $\text{H}_2^+$  and  $\text{H}_2$ . In the present note, similar calculations for two helium atoms are made.

To obtain the interactions between two helium atoms according to first principles, a practical procedure would be to calculate, for static nuclear configurations, the potential by the variational method with wave functions of the Hylleraas type. These wave functions contain as variables the distances  $r_{ij}$  between the electrons, thereby giving the "polarizability" of the atoms and the "dispersion" forces. Such a calculation would be very long on account of the large number (four) of electrons present. In the literature, calculations have been carried out with "product" wave functions to obtain the "valence" interaction, and on the basis of these wave functions, the dispersion interactions are calculated. It seems that a variational calculation even with product wave functions has not been carried out, and the most recent available calculation seems to be

that of Rosen<sup>2</sup> who employed a bond wave function constructed from single electron wave functions with fixed effective charges. In the previous note, it is pointed out that while the general repulsive character and the values of the coupling potential  $E^c(R)$  in the limiting cases of the united atom and the separated atoms are independent of the exact form of the wave function employed for the two interacting atoms, the exact values of  $E^c(R)$  for intermediate distances  $R$  do depend on the wave function, and for a given wave function of the variable effective charge type, on the value of the charge parameters at various distances  $R$ . The wave function of Rosen, constructed from the atomic wave functions of two free helium atoms, does not have variable parameters corresponding to the minimization of the energy of the diatomic system at various separations  $R$ . One may expect the valence repulsion between two helium atoms given by Rosen's wave function to be a fair approximation only for large separations  $R$ , since in the limit of the united atom, the wave function employed does not approach that of Be even in the matter of nodes. A more satisfactory, variational treatment of the problem of two helium atoms is certainly desirable, but obviously involves very lengthy calculations. While this is being attempted here, it is thought desirable to carry out the analytical part of the

<sup>1</sup> T. Y. Wu and A. B. Bhatia, *J. Chem. Phys.* **24**, 48 (1956).

<sup>2</sup> P. Rosen, *J. Chem. Phys.* **18**, 1182 (1950).

calculation of the coupling potential  $E^c(R)$  for two helium atoms on the basis of a wave function of the form of that of Rosen, in which the effective charges are regarded as parameters to be determined by a separate variational calculation. The result of these calculations may be expected to be a reasonable approximation for separations  $R$  not too small (as to approach the united atom), and not too large [when  $E^c(R)$  goes over into the inverse 8th power variation with  $R$ ], i.e., in the region where the usual Van der Waals' interaction is appreciable. This variational calculation, while lengthy, should be straightforward since the various integrals involved are already given in the paper of Rosen.

The wave function of Rosen<sup>2</sup> is

$$\Psi(1,2,3,4) = N[\psi_1 - \psi_2 - \psi_3 + \psi_4], \quad (1)$$

where  $N$  is the normalization factor and the  $\psi_i$  are determinantal wave functions.

$$\begin{aligned} \psi_1 &= |a\alpha \ b\beta \ c\alpha \ d\beta|, \\ \psi_2 &= |a\alpha \ b\beta \ c\beta \ d\alpha|, \\ \psi_3 &= |a\beta \ b\alpha \ c\alpha \ d\beta|, \\ \psi_4 &= |a\beta \ b\alpha \ c\beta \ d\alpha|. \end{aligned} \quad (2)$$

The  $a, b$  are hydrogenic  $1s$  wave functions referred to nucleus  $A$  and  $c, d$  referred to nucleus  $B$ . Thus

$$\begin{aligned} a(1)b(2) &= \exp[-(Z_1 r_{1A} + Z_2 r_{2A})/a], \\ c(3)d(4) &= \exp[-(Z_1 r_{3B} + Z_2 r_{4B})/a]. \end{aligned} \quad (3)$$

In Rosen's work, the effective charges  $Z_1, Z_2$  have the fixed values

$$Z_1 = 2.15, \quad Z_2 = 1.19. \quad (4)$$

In the present work these parameters are regarded as functions of  $R$ . The  $\alpha$  and  $\beta$  are the spin wave functions for  $m_Z = +\frac{1}{2}$  and  $-\frac{1}{2}$ , respectively. Let us also introduce the antisymmetric wave function

$$x_{ij} = (1/\sqrt{2})(\alpha_i \beta_j - \alpha_j \beta_i), \quad i \neq j = 1, 2, 3, 4, \quad (5)$$

which satisfy the following relations:

$$\int |x_{12}|^2 |x_{34}|^2 = \int |x_{23}|^2 |x_{14}|^2 = \int |x_{31}|^2 |x_{24}|^2 = 1,$$

and

$$\begin{aligned} \int x_{12}^* x_{34}^* x_{23} x_{14} &= \int x_{23}^* x_{14}^* x_{31} x_{24} \\ &= \int x_{12}^* x_{34}^* x_{31} x_{24} = -\frac{1}{2}. \end{aligned}$$

It can then be shown that  $\Psi(1,2,3,4)$  in (1) can be written in the form:

$$\begin{aligned} \Psi(1,2,3,4) &= \mathfrak{N} \phi = \mathfrak{N}(1 + Q_{13}Q_{12} + Q_{23}Q_{12}) \\ &\quad (1 + P_{13}P_{24})(1 + P_{12} + P_{34} + P_{12}P_{34}) \\ &\quad \times a(1)b(2)c(3)d(4)x_{12}x_{34}, \end{aligned} \quad (6)$$

where  $P_{ij}$  is an operator permuting only the space coordinates of the electrons  $i$  and  $j$ , and where  $Q_{ij}$  is an operator permuting both the space and the spin coordinates of the electrons  $i$  and  $j$ . It can be seen that  $\Psi$  in (6) is antisymmetric with respect to the interchange of any two electrons, but is also antisymmetric in the spin of two electrons referred to the same nucleus.

The "coupling potential" due to the coupling between the electronic and the nuclear motion is<sup>1</sup>

$$\begin{aligned} E^c(R) &= -\frac{\hbar^2}{2M} \int \Psi(\Delta_A + \Delta_B) \Psi d\tau \\ &= -\frac{\hbar^2}{M_{\text{He}}} \int \Psi(\tfrac{1}{4}\Delta_A + \Delta_R) \Psi d\tau, \end{aligned} \quad (7)$$

where  $\Lambda$  is the coordinate of the center of mass of the two nuclei, and  $R$  is the internuclear distance. On account of the normalization of  $\Psi$  for all nuclear coordinates, and the fact that the normalization constant  $\mathfrak{N}$  depends only on  $|R|$ , it can be shown that

$$\begin{aligned} \int \Psi(\tfrac{1}{4}\Delta_A + \Delta_R) \Psi d\tau &= \frac{1}{\mathfrak{N}} \frac{d^2 \mathfrak{N}}{dR^2} + \frac{2}{\mathfrak{N}R} \frac{d\mathfrak{N}}{dR} \\ &\quad - 2 \left( \frac{1}{\mathfrak{N}} \frac{d\mathfrak{N}}{dR} \right)^2 + \mathfrak{N}^2 \int \phi(\tfrac{1}{4}\Delta_A + \Delta_R) \phi d\tau. \end{aligned} \quad (8)$$

It can be shown that the  $24^2 = 576$  integrals in (8) reduce to 9 different integrals. After the differentiation with respect to  $\Lambda$  and  $R$ , the integrals are most conveniently evaluated by transforming to elliptic coordinates

$$R\xi_i = r_{iA} + r_{iB}, \quad R\eta_i = r_{iA} - r_{iB}, \quad i = 1, 2, 3, 4,$$

and

$$d\tau = \frac{R^{12}}{8^4} \prod_{i=1}^4 (\xi_i^2 - \eta_i^2) d\xi_i d\eta_i.$$

Writing

$$\lambda = Z_1 R/2a, \quad \mu = Z_2 R/2a, \quad (9)$$

then

$$\phi = \exp[-\lambda(\xi_1 - \eta_1) - \mu(\xi_2 - \eta_2) - \lambda(\xi_2 + \eta_3) - \mu(\xi_4 + \eta_4)].$$

Calculation leads to the following results:

$$(R^2/24) \int \phi(\tfrac{1}{4}\Delta_A + \Delta_R) \phi d\tau = A_1 + 2A_2 + A_3 + A_4 + 2A_5 + A_6 - 2(B_1 + 2B_2 + B_3), \quad (10)$$

where

$$A_1 = -(\lambda^2 + \mu^2)/4\lambda^6\mu^6, \quad A_2 = -8/\lambda^3\mu^3(\lambda + \mu)^4,$$

$$\begin{aligned}
A_3 &= -2 \times 32^2 \lambda \mu / (\lambda + \mu)^{12}, \quad A_4 = -FG(FC\mu^2 + GD\lambda^2)e^{-4(\lambda+\mu)}/4\lambda^6\mu^6, \\
F &= 1 + 2\lambda + (4\lambda^2/3), \quad G = 1 + 2\mu + (4\mu^2/3), \\
C &= 1 + 2\lambda - (4\lambda^2/3), \quad D = 1 + 2\mu - (4\mu^2/3), \\
A_5 &= -4e^{-2(\lambda+\mu)}K[\lambda e^{-2\mu} - \mu e^{-2\lambda} - 16(\lambda^4G + \mu^4F)K/3(\lambda^2 - \mu^2)]\lambda^3\mu^3(\lambda^2 - \mu^2)^3, \\
K &= \lambda e^{-2\mu} + \mu e^{-2\lambda} - (2\lambda\mu/(\lambda^2 - \mu^2))(e^{-2\mu} - e^{-2\lambda}), \\
A_6 &= 32^2 K^3[(\lambda^2 + \mu^2)K - (\lambda^2 - \mu^2)(\lambda e^{-2\mu} - \mu e^{-2\lambda})/2]/(\lambda^2 - \mu^2)^8, \\
B_1 &= -8e^{-2\lambda}\{\lambda[(\lambda + \mu)(1 + 2\lambda) - (4\lambda^2/3)(\lambda - \mu)]K + \mu(\lambda^2 - \mu^2)FE/2\}/\lambda^3\mu^3(\lambda^2 - \mu^2)^2(\lambda + \mu)^3, \\
E &= \frac{\lambda}{\lambda^2 - \mu^2}(e^{-2\mu} - e^{-2\lambda}) - e^{-2\lambda}, \\
B_2 &= -4K(\lambda e^{-2\mu} - \mu e^{-2\lambda})/\lambda^3\mu^3(\lambda^2 - \mu^2)^3, \\
B_3 &= 16e^{-2(\lambda+\mu)}[(\lambda - \mu)^2FG/2 - (1 + 2\lambda)\lambda^2G - (1 + 2\mu)\mu^2F]/\lambda^3\mu^3(\lambda + \mu)^6, \\
1/24\mathfrak{N}^2 &= \left(\frac{1}{4\lambda^3\mu^3} + \frac{16}{(\lambda + \mu)^6}\right)^2 + (FG e^{-2(\lambda+\mu)}/4\lambda^3\mu^3 + 16K^2/(\lambda^2 - \mu^2)^4)^2 - \frac{8e^{-2\lambda}FK}{\lambda^3\mu^3(\lambda + \mu)^3(\lambda^2 - \mu^2)^2} \\
&\quad - \frac{16K^2}{\lambda^3\mu^3(\lambda^2 - \mu^2)^4} - \frac{8e^{-2(\lambda+\mu)}FG}{\lambda^3\mu^3(\lambda + \mu)^6}. \quad (12)
\end{aligned}$$

On putting (8)–(12) into (7), one obtains the energy due to the coupling between the electronic and the nuclear motion of the system He-He.<sup>3</sup>

It is to be noted that in obtaining the expressions (11) for (10), terms arising from the variation of the parameters  $\lambda$  and  $\mu$  with the internuclear distance  $R$  have been neglected, although in the resulting expression (8) with the use of (11) and (12), the appropriate values for  $\lambda$  and  $\mu$  must be used for various distances  $R$ . The functions  $\lambda(R)$  and  $\mu(R)$  have to be determined by carrying out a separate variational calculation for the He-He system (for fixed  $R$ ) for various values of  $R$ . While the quantitative results on  $E^c(R)$  depend on the  $\lambda(R)$  and  $\mu(R)$  of this calculation, the qualitative result can be stated as follows. Asymptotically for large  $R$ , it can be shown from (8)–(12) that

$$\begin{aligned}
E^c(\infty) &= \frac{\hbar^2}{M_{\text{He}} a^2} \left[ \frac{Z_1^2 + Z_2^2}{Z_1^6 Z_2^6} + \frac{64}{Z_1^3 Z_2^3 (Z_1 + Z_2)^4} \right. \\
&\quad \left. + \frac{2 \times 64^2 Z_1 Z_2}{(Z_1 + Z_2)^{12}} \right] \left[ \frac{1}{Z_1^3 Z_2^3} + \frac{64}{(Z_1 + Z_2)^6} \right]^2 \\
&= 4 \cdot 1.685^2 \left( \frac{m}{M_{\text{He}}} \right) \frac{\hbar^2}{2ma^2}, \quad (13)
\end{aligned}$$

<sup>3</sup> Note added in proof.—It must be remembered that the asymptotic form of  $E^c(R)$  for large  $R$  as given by (10)–(12) is not correct, and must be replaced by an inverse eighth power variation in  $R$ .<sup>1</sup>

which is seen to be the sum of the corrections, for the two free He atoms, for the relative motion between the nucleus (of mass 4) and the two hydrogenic electrons each with the effective charge 1.685e. If instead of (4) one works with  $Z_1 = Z_2$ , then (13) becomes

$$E^c(\infty) = 4 \left( \frac{m}{M_{\text{He}}} \right) \left( \frac{Z^2 \hbar^2}{2ma^2} \right).$$

The relevant correction, in so far as the interaction between two helium atoms is concerned, is

$$\Delta E^c(R) = E^c(R) - E^c(\infty).$$

For  $R=0$ , the wave function (1)–(3) does not give exactly the correct value for the relative motion correction for the united atom, for the reason given earlier in the present note. For intermediate distances  $R$ ,  $\Delta E^c(R)$  is a repulsive potential, whose exact values await the variational calculation of  $Z_1(R)$ ,  $Z_2(R)$ . That this coupling potential  $\Delta E^c(R)$  is inversely proportional to the reduced mass of the two atoms shows that this coupling, in addition to the mass factor in the Schrödinger equation for the relative motion of the two atoms, contributes to a weaker binding between two He<sup>3</sup> atoms compared with two He<sup>4</sup> atoms.