

ON THE ELECTRONIC ENERGY OF A ONE-ELECTRON DIATOMIC
MOLECULE NEAR THE UNITED ATOM *

by

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ABSTRACT

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The behaviour of the electronic energy for the ground state of a one-electron heteronuclear diatomic molecule in the vicinity of the united atom is obtained through terms of order R^5 in the internuclear distance R . The presence of a term in $R^5 \log R$ reveals that the electronic energy is not an analytic function of R at the united atom. The expansion is checked by means of the Hellmann-Feynman theorem and the work of Dalgarno and Lynn.

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PREFACE

This report is a revised and extended version of WIS-TCI-33. The extension is from terms of order R^4 to terms of order R^5 in the electronic energy as a function of internuclear distance R . The chief revisions are:

- (i) simpler definition of the separation constant C ;
- (ii) re-definition of the heterogeneity index k ;
- (iii) use of a three-term, rather than a five-term, recursion relation for the coefficients in the solution of the inner equation.

INTRODUCTION

The total energy of a diatomic molecule AB in a stationary electronic state with fixed internuclear separation R may be written

$$E(R) = W(R) + Z_a Z_b / R, \quad (1)$$

where W is the electronic energy and Z_a, Z_b are the atomic numbers of the nuclei. Since the electronic energy is finite for all values of R it is natural to assume that it is analytic and may be expanded about $R = 0$ in powers of R :

$$W(R) = W_0 + RW_1 + R^2 W_2 + R^3 W_3 + R^4 W_4 + \dots \quad (2)$$

The leading term $W_0 = W(0)$ is the energy of the united atom with atomic number $Z = Z_a + Z_b$, and R. A. Buckingham¹ pointed out that the first coefficient W_1 always vanishes exactly, even for many-electron heteronuclear molecules.

The second coefficient was obtained by Bingel² from a first-order perturbation treatment based on the united atom, and is given by (atomic units)

$$W_2 = \frac{Z_a Z_b}{Z} \left[\frac{2}{3} \pi \rho_{UA}(0) - \frac{1}{2} \int P_2(\cos\theta) r^{-3} \rho_{UA}(r) d\tau \right], \quad (3)$$

where $\rho_{UA}(r)$ is the electron density of the united atom; the second term in the bracket is essentially the field gradient at the nucleus, and vanishes for an S-state. Bingel also obtained a general expression for the third coefficient W_3 from his first-order treatment, by arguing that the second-order perturbation energy would be of order R^4 and contribute only to W_4 and higher terms. However, earlier work by the authors³ on the one-electron case, which may be analyzed explicitly, showed that Bingel's formula was incorrect. More recently, Levine⁴ has obtained the second-order energy explicitly for a homonuclear one-electron molecule, and shown that it is of order R^3 . It appears to be extremely difficult to analyze the second-order perturbation energy in the general case of a many-electron molecule. However, the form of W_3 in the general case has recently been derived⁵ by an alternative route based on the Hellmann-Feynman expression for the force dW/dR , and is given by

$$W_3 = -Z_a Z_b \frac{2}{3} \pi \rho_{UA}(0). \quad (4)$$

It is of great interest to know the general form of the higher terms in equation (2). As a first step it seems prudent to carry the explicit analysis of the ground state of the one-electron system further, and this is the object of the present paper.

ELECTRONIC ENERGY

The electronic energy $W(R, Z_a, Z_b)$ possesses two simple features as a function of R, Z_a, Z_b . The first is symmetry with respect to the interchange of nuclei A and B, and is true for many-electron molecules:

$$W(R, z_a, z_b) = W(R, z_b, z_a). \quad (5)$$

The second property, peculiar to one-electron molecules, is that

W is homogeneous and of degree two in Z_a, Z_b and $1/R$. In view of these features, W may be written in the form

$$W(R, z_a, z_b) = z^2 w(Rz, z_az_b/z^2). \quad (6)$$

There are, therefore, essentially only two independent variables in W . The limiting values for the ground state of the molecule are:

- (a) United atom, $R = 0$: $W = -\frac{1}{2} z^2$.
- (b) Separated atoms, $R = \infty$: $W = -\frac{1}{2} z_a^2$ ($z_a > z_b$)
- (c) Atom A, $Z_b = 0$: $W = -\frac{1}{2} z_a^2$; similarly for B.

Certain other features of W are known.

(a) As mentioned above, the force between the nuclei due to the electronic motion vanishes at the united atom, so that

$$\left(\frac{\partial W}{\partial R}\right)_{R=0} = W_1 = 0. \quad (7)$$

(b) By the Hellmann-Feynman theorem

$$\left(\frac{\partial W}{\partial Z_b}\right)_{Z_b=0} = \phi_a(R) \quad (8)$$

where $\phi_a(R)$ is the electrostatic potential due to atom A at distance R from the nucleus and is given by

$$\phi_a(R) = - \int \frac{\rho_a(r)}{|r - R|} d\tau, \quad (9)$$

where $\rho_a(r)$ is the electron density of atom A.

(c) The perturbation of the one-electron atom A by a charge Z_b at distance R can be treated analytically. The first-order energy is precisely equation (8). The second-order energy is

$$\frac{1}{2} \left(\frac{\partial^2 W}{\partial Z_b^2}\right)_{Z_b=0},$$

and has been obtained by Dalgarno and Lynn⁶, and by Robinson⁷.

Their work can therefore be used to check the results obtained in the present paper.

SCHRODINGER EQUATION

The Schrodinger equation for the system (atomic units),

$$\left(\frac{1}{2} \nabla^2 + \frac{z_a}{r_a} + \frac{z_b}{r_b} + W \right) \psi = 0, \quad (10)$$

may be separated by introducing confocal elliptic (prolate spheroidal) coordinates ξ , η , ϕ , the first two being defined by

$$\xi = (r_a + r_b)/R, \quad \eta = (r_a - r_b)/R, \quad (11)$$

and ϕ being the azimuthal angle. For Σ states, which are axially symmetric, the wave function may be written in the form

$$\psi = H(\eta) X(\xi). \quad (12)$$

The functions H and X satisfy the 'inner' and 'outer' equations

$$\frac{d}{d\eta} \left[(1-\eta^2) \frac{dH}{d\eta} \right] + \left[-2p^2\eta - p^2(1-\eta^2) + C \right] H = 0$$

$$(-1 \leq \eta \leq 1), \quad (13)$$

$$\frac{d}{d\xi}[(\xi^2-1)\frac{dX}{d\xi}] + [2p(1+\sigma)\xi - p^2(\xi^2-1) - C]X = 0$$

$$(1 \leq \xi \leq \infty), \quad (14)$$

where (assuming a bound state, $W < 0$) the parameters σ , p and k can be thought of as corresponding to W/Z^2 , RZ and $Z_a Z_b / Z^2$, and are defined by

$$p^2 = -\frac{1}{2} R^2 W, \quad (15)$$

$$1+\sigma = RZ/2p, \quad (16)$$

$$k = R(z_a - z_b)/2p. \quad (17)$$

The differential equations (13) and (14) only have square-integrable solutions if the separation constant C has certain functional forms, say $C_{\text{inner}}(p, k)$ and $C_{\text{outer}}(p, \sigma)$. The relations between the parameters σ , p and k , which are equivalent to the electronic energy eigenvalues W as functions of RZ and $Z_a Z_b / Z^2$, are then given by the equations

$$C_{\text{inner}}(p, k) = C_{\text{outer}}(p, \sigma). \quad (18)$$

The procedure we shall follow to obtain the dependence of W on R when R is small is essentially that introduced by

Hylleraas⁸ in solving the equations to any accuracy. The function $H(\eta)$ is expanded in terms of Legendre polynomials, and from the resulting determinant of elimination the separation eigen-constant C_{inner} can be expressed as a power series in p^2 . The outer equation for $X(\xi)$ can be treated in a similar fashion, but the determinant of elimination cannot be expanded indefinitely as a power series in p and σ . It is then expedient to return to the differential equation and solve it in an iterative manner to obtain the non-analytic terms.

INNER EQUATION

The mathematical properties of this equation are well-known⁹.

It is convenient to put

$$H(\eta) = e^{\pm p\eta} h(\eta), \quad (19)$$

where the sign of the exponent is unimportant for our purposes; for definiteness we take the positive sign. Then $h(\eta)$ satisfies

$$\frac{d}{d\eta} \left[(1-\eta^2) \frac{dh}{d\eta} \right] + 2p(1-\eta^2) \frac{dh}{d\eta} + [C - 2p(1+k)\eta] h = 0. \quad (20)$$

Consider a solution of (20) in the form^{8,9}

$$h(\eta) = \sum_{l=0}^{\infty} h_l P_l(\eta), \quad (21)$$

where $P_l(\eta)$ is the l th Legendre polynomial. By substituting (21) into (20) and using the differential equation and recurrence relations for P_l we get¹⁰

$$2p \frac{(l+1)(l+1-k)}{(2l+3)} h_{l+1} + [C - l(l+1)] h_l - 2p \frac{l(l+k)}{(2l-1)} h_{l-1} = 0$$

$$(l = 0, 1, 2, \dots), \quad (22)$$

with $h_{-1} \equiv 0$ and h_0 arbitrary. This is a three-term recurrence relation for the coefficients h_l . The condition that the infinite series solution (21) is square-integrable is that the determinant of elimination vanishes, namely

$$\begin{vmatrix} C & 2p(1-k)/3 & 0 & 0 & \cdot \\ -2p(1+k) & C-2 & 4p(2-k)/5 & 0 & \cdot \\ 0 & -4p(2+k)/3 & C-6 & 6p(3-k)/7 & \cdot \\ 0 & 0 & -6p(3+k)/5 & C-12 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{vmatrix} = 0 \quad (23)$$

Before considering the solution of (23), it is helpful to make the following remark. The "heterogeneity" parameter k defined by equation (17) can be written in the form

$$k^2 = (1 - 4z_a z_b / z^2)(z^2 / -2w). \quad (24)$$

It follows that when the system reduces to atom A ($z_b = 0$) or atom B ($z_a = 0$) in the electronic state with quantum numbers ($n l 0$), $k = n$ or $-n$ irrespective of the value of R (and therefore of p). Now the separation constant C vanishes for the ground state of the atoms, that is when $k = \pm 1$. Therefore, the ground state eigen-constant C_{inner} satisfying equation (23) must have $(1 - k^2)$ as a factor; this conclusion can be confirmed by inspection.

We are interested in solving equation (25) for small values of R , that is of p . Expanding the determinant we have

$$C \Delta_1 + \frac{4}{3} p^2 (1 - k^2) \Delta_2 = 0 \quad (25)$$

where Δ_1 , and Δ_2 , are the principal minors obtained by deleting the first, and the first two, rows and columns.

When $p \rightarrow 0$

$$\Delta_1 / \Delta_2 = -2 + O(p^2),$$

and, hence the first approximation for C is

$$C_{\text{inner}} = \frac{2}{3} p^2 (1 - k^2) + O(p^4). \quad (26)$$

Now

$$\Delta_1 = (C-2)\Delta_2 + \frac{16}{15}p^2(4-k^2)\Delta_3,$$

and therefore by substituting in (25) and noting that

$$\Delta_2/\Delta_3 = -6 + O(p^2),$$

the second approximation is

$$C_{inner} = (1-k^2) \left[\frac{2}{3}p^2 - \frac{2}{135}p^4(1+11k^2) + O(p^6) \right]. \quad (27)$$

It is clear that the solutions $C_{inner}(p,k)$ of equation (23) can be written as infinite power series in p^2 . The higher terms are readily obtained but will not be considered here.

OUTER EQUATION

To solve the outer equation systemically we follow Jaffe¹¹ and put

$$X = e^{-p\zeta} (1+\zeta)^\sigma F, \quad (28)$$

and change to the variable

$$\zeta = \frac{\xi-1}{\xi+1}, \quad (0 \leq \xi \leq 1). \quad (29)$$

The function $F(\zeta)$ satisfies the equation

$$\begin{aligned} \zeta(1-\zeta)^2 \frac{d^2 F}{d\zeta^2} + [1 + 2(\sigma - 2p - 1)\zeta + (1 - 2\sigma)\zeta^2] \frac{dF}{d\zeta} \\ + [\sigma(1 + 2p) - C + \sigma^2 \zeta] F = 0, \end{aligned} \quad (30)$$

and may be expressed as the power series

$$F = \sum_{n=0}^{\infty} c_n \zeta^n. \quad (31)$$

The coefficients in equation (31) satisfy the three-term recurrence relation

$$\begin{aligned} (n+1)^2 c_{n+1} + [A - \sigma^2 - 2n(n+2p-\sigma)] c_n + (n-1-\sigma)^2 c_{n-1} = 0, \\ (n = 0, 1, 2, \dots), \end{aligned} \quad (32)$$

where $c_{-1} \equiv 0$, we can take $c_0 = 1$, and we have put

$$A = \sigma(1 + 2p) + \sigma^2 - C. \quad (33)$$

The condition that the infinite series solution (31) is square-integrable is that determinant of elimination vanishes, namely

$$\begin{vmatrix} A - \sigma^2 & 1^2 & 0 \\ \sigma^2 & A - \sigma^2 - 2(1+2p - \sigma) & 2^2 \\ 0 & (1 - \sigma)^2 & A - \sigma^2 - 4(2+2p - \sigma) \end{vmatrix} = 0 \quad (34)$$

Before proceeding further it is necessary to know the order of magnitude of the energy parameter σ , in terms of which the electronic energy is

$$W = -Z^2/2(1+\sigma)^2. \quad (35)$$

It follows that for the united atom ($p=0$) in the electronic state $(n \neq 0)$, $\sigma = n-1$. It is then easy to see that $\sigma = 0(p^2)$ for the ground state of interest.

Returning to the determinantal equation (34), it is obvious that $A = 0(\sigma^2) = 0(p^4)$. To proceed further requires some care. Let us focus attention on the leading term in A , which is of order p^4 or higher. Then we can replace equation (34) by

$$\begin{vmatrix}
 A - \sigma^2 & 1^2 & 0 & \cdot \\
 \sigma^2 & -2(1+2p) & 2^2 & \cdot \\
 0 & 1^2 & -4(2+2p) & \cdot \\
 \cdot & \cdot & \cdot & \cdot
 \end{vmatrix} \approx 0, \quad (36)$$

which is equivalent to

$$\begin{vmatrix}
 A - \sigma^2 & -1 & 0 & 0 & \cdot \\
 \sigma^2 & 2(1+2p) & -1 & 0 & \cdot \\
 0 & -1 & 2(1+2p/2) & -1 & \cdot \\
 0 & 0 & -1 & 2(1+2p/3) & \cdot \\
 \cdot & \cdot & \cdot & \cdot & \cdot
 \end{vmatrix} \approx 0. \quad (37)$$

This determinant may be expanded as a continued fraction to give

$$A \approx \sigma^2 \left[1 - \frac{1}{2(1+2p)} - \frac{1}{2(1+2p/2)} - \frac{1}{2(1+2p/3)} - \dots \right]. \quad (38)$$

To find the term of order σ^2 we set $p = 0$ in the continued fraction to get¹²

$$A = \sigma^2 \left[1 - \frac{1}{2-} \frac{1}{2-} \frac{1}{2-} \dots \right] + o(p^4). \quad (39)$$

The coefficient of σ^2 is $1-\alpha$ where

$$\alpha = \frac{1}{2-} \frac{1}{2-} \frac{1}{2-} \dots = \frac{1}{2-\alpha}.$$

Thus $\alpha = 1$ and the term in σ^2 vanishes. Hence $A = o(p^4)$, or in terms of the original separation constant

$$C_{outer} = \sigma(1+2p) + \sigma^2 + o(p^4). \quad (40)$$

At this stage, by equating C_{inner} from equation (27) and C_{outer} from equation (40), according to equation (18), the expansion of W in powers of R through R^4 may be found. The next term may no doubt be obtained by investigating the continued fraction in equation (38). However, as the analysis required is not familiar, and the form is not quoted in the readily accessible literature, we have found it simpler to return to the differential equation.

ANALYSIS OF DIFFERENTIAL EQUATION

The differential equation (30) for F may be written in the form

$$\frac{d}{d\zeta} \left(\zeta \frac{dF}{d\zeta} \right) + \left[-\frac{4p}{(1-\zeta)^2} + \frac{2\sigma}{1-\zeta} \right] \zeta \frac{dF}{d\zeta} + \left[\frac{A}{(1-\zeta)^2} - \frac{\sigma^2}{1-\zeta} \right] F = 0. \quad (41)$$

The discussion above has established that

$$\sigma = O(p^2) \text{ and } A = o(p^4),$$

and it is then evident from the recurrence relation (32) that

$c_n = O(\sigma^2)$ for $n > 0$. We therefore put

$$F = 1 + \sigma^2 f \quad (42)$$

where

$$f(\zeta=0) = 0. \quad (43)$$

Equation (41) can then be written

$$\begin{aligned} \frac{d}{d\zeta} \left(\zeta \frac{df}{d\zeta} \right) + \left[-\frac{4p}{(1-\zeta)^2} + \frac{2\sigma}{1-\zeta} \right] \zeta \frac{df}{d\zeta} + \frac{B}{(1-\zeta)^2} - \frac{1}{1-\zeta} \\ = -\sigma^2 \left[\frac{B}{(1-\zeta)^2} - \frac{1}{1-\zeta} \right] f, \end{aligned} \quad (44)$$

where $B = \sigma^{-2}A = o(1)$. We shall now proceed to solve this equation with increasing degrees of accuracy.

(a) Retain $O(1)$

If terms involving σ^2 , σ , p and B are dropped from equation (44) we are left with

$$\frac{d}{dz} \left(z \frac{df}{dz} \right) - \frac{1}{1-z} \cong 0. \quad (45)$$

Hence, by two quadratures

$$f \cong - \int_0^z \log(1-x) d \log x = \text{Li}_2(z), \quad (46)$$

where Li_2 is the dilogarithm function¹³. The wave function X , given by equations (28) and (42), therefore has the form

$$X(z) = e^{-pz} (1+z)^\sigma \left[1 + \sigma^2 \text{Li}_2\left(\frac{z-1}{z+1}\right) + o(p^4) \right]. \quad (47)$$

(b) Retain $O(p)$

If terms involving σ^2 and σ are omitted from equation (44) it becomes

$$\frac{d}{dz} \left(z \frac{df}{dz} \right) - \frac{4p}{(1-z)^2} z \frac{df}{dz} \cong \frac{1}{1-z} - \frac{B}{(1-z)^2}. \quad (48)$$

This equation may be integrated once to give

$$\xi \frac{df}{d\xi} \cong \exp\{4p/(1-\xi)\} \int_1^{(1-\xi)^{-1}} e^{-4pt} (t^{-1} - B) dt.$$

By changing back to the variable ξ and splitting the integral, we get

$$\begin{aligned} \frac{df}{d\xi} \cong & 2(\xi^2-1)^{-1} \left\{ e^{2p(\xi+1)} [ei(4p) - B e^{-4p/4p}] + \right. \\ & \left. + [B/4p - e^{2p(\xi+1)} ei\{2p(\xi+1)\}] \right\}, \end{aligned} \quad (49)$$

where

$$ei(x) = \int_x^\infty e^{-t} t^{-1} dt. \quad (50)$$

Now the function f must not increase with ξ as fast as $\exp(p\xi)$, otherwise by equations (28) and (42) the function $X(\xi)$ will not be $L^2(1, \infty)$. But unless the coefficient of $\exp\{2p(\xi+1)\}$ in equation (49) vanishes, f will increase like $\exp(2p\xi)$. Hence we must have

$$B = 4p e^{4p} ei(4p) + o(p). \quad (51)$$

Now

$$ei(x) = -\log x + x + O(x^2)$$

where $\log \gamma$ is Euler's constant. Therefore

$$B = 4p \log p + 4p \log 4\gamma + o(p). \quad (52)$$

The function f may be obtained to this order of accuracy by integrating equation (49), but is not quoted since the integral cannot be expressed in terms of familiar functions.

(c) Neglect σ^2

If only the term in σ^2 is neglected, equation (44) may still be integrated once to give

$$\zeta \frac{df}{d\zeta} \cong [2p(\zeta+1)]^{-\sigma} \exp[2p(\zeta+1)] \left\{ \int_{4p}^{\infty} e^{-x} (x^{-1} - B/4p) x^{2\sigma} dx - \int_{2p(\zeta+1)}^{\infty} e^{-x} (x^{-1} - B/4p) x^{2\sigma} dx \right\}. \quad (53)$$

By the same argument as above, in order for $X(\zeta)$ to be square integrable the first integral in the parentheses must vanish. Hence

$$B = 4p \Gamma(2\sigma, 4p) / \Gamma(2\sigma+1, 4p) + o(p^3), \quad (54)$$

where $\Gamma(y, x)$ is the incomplete gamma function¹⁴ defined by

$$\Gamma(y, x) = \int_x^{\infty} e^{-t} t^{y-1} dt. \quad (55)$$

Clearly, by letting $\sigma \rightarrow 0$ in equation (54) we return to equation (51). Higher terms in f and B can presumably be found by solving equation (53) for f , substituting on the right hand side of (44) and integrating to find a new expression for f .

ENERGY EXPANSION

The separation eigen-constant obtained from the outer equation in the previous sections may be written

$$C_{\text{outer}} = \sigma(1+2p) + \sigma^2 [1 + 4p \log 4p] + o(p^5). \quad (56)$$

The relation between σ , p and k for the ground state is obtained by equating this to C_{inner} , given by equation (27), namely

$$C_{\text{inner}} = (1-k^2) \left[\frac{2}{3} p^2 - \frac{2}{135} p^4 (1+11k^2) \right] + O(p^6). \quad (57)$$

To find the expansion of W in powers of R through $O(R^5)$, or more conveniently in powers of $s = R^2$, we proceed as follows. Since $\sigma = O(s^2)$, equation (35) can be expanded to give

$$W = -\frac{1}{2} z^2 (1 - 2\sigma - 3\sigma^2) + O(s^6). \quad (58)$$

We seek the expansion of σ in powers of s by substituting

$$p = \frac{1}{2} s (1 + \sigma)^{-1} \quad (59)$$

and

$$k^2 = (1 - \beta)(1 + \sigma)^2, \quad (60)$$

where $\beta = z_a z_b / z^2$, into equations (56) and (57).

By ignoring terms of $o(s^5)$ this yields

$$\sigma(1 + s - \frac{1}{3}s^2) + \sigma^2(1 - s + 2s \log 2s\gamma) = \frac{1}{6}\beta s^2 - \frac{\beta s^4}{1080}(12 - 11\beta) + o(s^5). \quad (61)$$

By solving iteratively for σ and substituting the result into equation (58) we obtain finally

$$W = -\frac{1}{2}z^2 \left[1 - \frac{1}{3}\beta s^2 + \frac{1}{3}\beta s^3 - \frac{1}{5}\beta(1 - 16\beta/27)s^4 + \right. \\ \left. + \frac{\beta}{45} \{ 5\beta \log(2s\gamma) + 4 - 199\beta/12 \} s^5 + o(s^5) \right]. \quad (62)$$

or

$$W = -\frac{1}{2}z^2 + \frac{2}{3}z_a z_b (Rz)^2 - \frac{2}{3}z_a z_b (Rz)^3 + \frac{2}{5}z_a z_b (1 - 64z_a z_b / 27z^2)(Rz)^4 \\ - \frac{8z_a z_b}{45} \left[\frac{5z_a z_b}{z^2} \log(2Rz\gamma) + 1 - \frac{199z_a z_b}{12z^2} \right] (Rz)^5 + o(R^5). \quad (63)$$

The occurrence of the term in $R^5 \log R$ reveals the interesting

fact that the electronic energy is not an analytic function of the internuclear distance at $R = 0$. This result must also be true in the many-electron case; and presumably neither is the electronic energy of polyatomic molecules an analytic function of the various internuclear distances at the united atom. The logarithmic term can be regarded as a consequence of the coulombic singularities in the potential. It does not appear in Frost's one-dimensional model in which the electron is attracted to the nuclei by delta potentials. It is obvious from equation (61) that higher terms in the expansion will also involve $\log R$, and it can easily be seen from equation (54) for B that a term in $R^7(\log R)^2$ will also occur.

The dependence of W on $z_a z_b / z^2$ is interesting. It is clear from the dependence of C_{inner} on k^2 , which involves $\beta = 4z_a z_b / z^2$ linearly, that W can be expanded in a power series in β about $\beta = 0$. Equation (6) may therefore be written in the form

$$W = z^2 \sum_{n=0}^{\infty} (z_a z_b / z^2)^n w_n(Rz). \quad (64)$$

The coefficient $w_1(Rz)$ is a first-order energy, and can be given explicitly in closed form. It is analytic in Rz at $R = 0$. The first logarithmic term occurs in w_2 , which is also known explicitly in closed form. A noteworthy feature of the expansion (64) is that

$$w_n(Rz) = O(R^{2n}). \quad (65)$$

This is clearly true for w_1 and w_2 from equation (63). The general result follows from the fact that s^2 is the lowest power of $s = RZ$ associated with β in C_{inner} , given by equation (57), and in general by equation (23). One would expect (65) this to be true also in the many-electron case, where the coefficients $w_n = w_n(RZ, 1/Z)$ depend also on $1/Z$ because of electronic repulsion.

DISCUSSION

1. Coefficient W_2

It follows from equation (63) by comparison with equation (2) that

$$W_2 = \frac{2}{3} z_a z_b z^2. \quad (66)$$

This agrees with the result obtained from the general formula (3) by inserting $\rho_{\text{UA}}(0)$ for the ground state (1s) of a one-electron atom, namely Z^3/π , and setting the field gradient equal to zero.

2. Coefficient W_3

From (63) we have

$$W_3 = -\frac{2}{3} z_a z_b z^3, \quad (67)$$

which agrees with the general formula (4). However, it does not agree with Bingel's² original formula, which had the wrong dependence on $z_a z_b / z^2$, namely

$$\begin{aligned} W_3(\text{Bingel}) &= -\frac{2}{3} z_a z_b (z_a^2 + z_b^2) z, \\ &= -\frac{2}{3} (z_a z_b / z^2) (1 - 4 z_a z_b / z^2) z^5. \end{aligned} \quad (68)$$

3. Hellmann-Feynman Theorem

For a one-electron atom in the ground state equations (8) and (9) become

$$\begin{aligned} \left(\frac{\partial W}{\partial z_b} \right)_{z_b=0} &= (z_a + 1/R) \exp(-2z_a R) - 1/R, \\ &= -z_a \left[1 - \frac{2}{3} (Rz_a)^2 + \frac{2}{3} (Rz_a)^3 - \frac{2}{5} (Rz_a)^4 + \frac{8}{45} (Rz_a)^5 - \dots \right]. \end{aligned} \quad (69)$$

An identical expression is obtained by differentiating equation (63) with respect to z_b .

4. Perturbation of atom A by charge z_b

As mentioned earlier, the perturbation of a one-electron atom, with atomic number z_a , by a charge z_b at distance R , can be treated analytically. The second order energy is^{6,7}

$$\begin{aligned}
 W^{(2)} = \frac{1}{2} \left(\partial^2 W / \partial z_b^2 \right)_{z_b=0} &= 2x^{-2} \left[5 - (x^2 + 4x + 10)e^{-x} \right. \\
 &+ (x^3/2 + 7x^2/4 + 4x + 5)e^{-2x} \\
 &+ 2(x/2 + 1)^2 e^{-x} (1 + e^{-x}) \{ e^{i(-x)} + 2 \log(xy) \} \\
 &\left. + 2 \{ (x/2 - 1)^2 e^x + x^2/4 + x - 3 + 2(x+2)e^{-x} \} e^{i(x)} \right],
 \end{aligned}
 \tag{70}$$

where $x = 2RZ_a$. When this expression is expanded in powers of x we get

$$\begin{aligned}
 W^{(2)} = -\frac{1}{2} + \frac{1}{3}x^2 - \frac{1}{4}x^3 + \frac{11}{270}x^4 - \frac{x^5}{36} \log(xy) \\
 + \frac{139}{2160}x^5 + o(x^5).
 \end{aligned}
 \tag{71}$$

An identical expression is obtained for the coefficient of z_b^2 from equation (63).

5. United atom perturbation treatment

Levine has evaluated the second-order energy $E^{(2)}$ in closed form for the perturbation treatment of a homonuclear one-electron molecule (H_2^+) based on the united atom at the centre of charge (mid-point). The first-order energy in this treatment is ($s = RZ$)

$$\begin{aligned}
 E^{(1)} &= z^2 [1 + e^{-s} - 2(1 - e^{-s})/s], \\
 &= z^2 \left[\frac{1}{6}s^2 - \frac{1}{12}s^3 + \frac{1}{40}s^4 + O(s^5) \right].
 \end{aligned}
 \tag{72}$$

The expansion of the second-order energy quoted by Levine⁴ is

$$E^{(2)} = Z^2 \left[-\frac{1}{12} s^3 - \frac{11}{2160} s^4 - \frac{s^5}{36} \log s + O(s^5) \right]. \quad (73)$$

By combining (72) and (74), and including the zeroth-order energy, we obtain

$$W_0 + E^{(1)} + E^{(2)} = Z^2 \left[-\frac{1}{2} + \frac{1}{6} s^2 - \frac{1}{6} s^3 + \frac{43}{2160} s^4 - \frac{1}{36} s^5 \log s + O(s^5) \right]. \quad (74)$$

The expansion (62) for the homonuclear case ($\beta = 1$) is

$$W = Z^2 \left[-\frac{1}{2} + \frac{1}{6} s^2 - \frac{1}{6} s^3 + \frac{11}{270} s^4 - \frac{1}{18} s^5 \log s + O(s^5) \right]. \quad (75)$$

We see that the united atom perturbation treatment through $E^{(2)}$ gives the correct numerical coefficients for R^2 and R^3 , but not those for the terms R^4 and $R^5 \log R$. We deduce that $E^{(3)}$ is of order R^4 , and probably contains a logarithmic term.

It appears to be very difficult to predict the order in R of the perturbation energies $E^{(n)}$ for this treatment.

CONCLUSIONS

The most striking result is the presence of logarithmic terms in the electronic energy of a molecule near the united atom. This

may be compared with the presence of exponentially small terms in R , as well as inverse powers of R , in the asymptotic behaviour of the electronic energy near infinite separation. The leading exponential terms have recently been obtained explicitly for a homonuclear one-electron molecule by Orchinnikov and Sukhanov¹⁵. However, the physical origin of the two kinds of terms is quite different.

The other result of interest is the simplicity of the expansion (64) of W in powers of $Z_a Z_b / Z^2$, as revealed by (65). In this expansion the term R^4 appears as the leading second-order term, in contradistinction to the united atom perturbation treatment. Although it is not possible to write the molecular Hamiltonian with $Z_a Z_b / Z^2$ as a linear perturbation parameter, the coefficients w_n in (64) are simply related to a finite sum of the perturbation energies associated with the perturbation of an atom by a small charge, Z_b , at distance R . It follows that if (65) is true in the many-electron case, the coefficient W_4 and the higher terms of equation (2) may be obtained by considering the perturbation of an atom by a small charge. This is equivalent to a united atom perturbation treatment in which the united atom remains at one of the nuclei, instead of being placed at the centre of nuclear charge.

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