Theoret. chim. Acta (Berl.) 4, 393—407 (1966)

Commentationes

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A Perturbation Theory of Isoelectronic Molecules: Application to CO Based on N_2*

By

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A perturbation theory of heteronuclear diatomic molecules based on the isoelectronic homonuclear molecules is developed for calculating the molecular energy, equilibrium internuclear distance, dissociation energy, and electric dipole moment.

The theory is applied to the isoelectronic molecules CO and N_2. The uncoupled Hartree-Fock approximation to the first-order perturbed wavefunction is determined by the variational method. The calculated molecular energy of CO is too low and the dipole moment is too large in magnitude. However, the calculated polarity is in agreement with the results of recent Hartree-Fock calculations at the equilibrium distance.

Moleküle aus zwei verschiedenen Atomen werden als gestörte gleichkernige, isoelektronische Moleküle behandelt, um Energie, Gleichgewichtskernabstand, Dissoziationsenergie und Dipolmoment zu berechnen.

Das Verfahren wird auf das Paar CO, N_2 angewandt. Die ungekoppelte Hartree-Fock-Näherung für die gestörte Funktion erster Ordnung wird durch Variation bestimmt. Für CO errechnen sich eine zu niedrige Energie und ein zu großes Dipolmoment, dessen Richtung mit der aus neueren Hartree-Fock-Rechnungen für den Gleichgewichtsabstand erhaltenen übereinstimmt.

On développe un procédé où les molécules diatomiques hétéronucléaires sont traitées comme molécules homonucléaires isoélectroniques perturbées, et on calcule l'énergie moléculaire, la distance d'équilibre des noyaux, l'énergie de dissociation et le moment dipolaire.

Ce procédé est appliqué à CO et N_2. L'approximation Hartree-Fock non-couplée pour la fonction d'onde perturbée de premier ordre, est déterminée par variation. L'énergie calculée pour CO est trop basse, le moment dipolaire étant trop haut. Cependant, sa direction s'accorde aux résultats de calculs Hartree-Fock récents pour la distance d'équilibre.

I. Introduction

The motivation for this investigation is the desire to compare the molecules CO and N_2, to understand their differences, and in particular the electric dipole moment of CO and its sign. The striking similarity of the two molecules can be seen from Tab. 1: the bond distances differ by only 3 per cent, and although the dissociation energies differ by about 13 per cent, the total molecular energies are within 3.5 per cent of each other. The polarity of the dipole moment of CO is very difficult to determine, but was deduced indirectly to be $C^- O^+$ from microwave measurements of rotational magnetic moments and $J = 1 \leftarrow 0$ rotational frequencies for various isotopic species of CO [*18*]. However, despite the initial support of this result by Ransil's Hartree-Fock calculation [*16*] using a minimum basis set,

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* This research was supported by the National Aeronautics and Space Administration Grant NsG-275-62.

Table 1. *Experimental properties of nitrogen and carbon monoxide*

	R_e (Å)	E_e (H)	D_e (eV)	k_e (10^6 dyne cm^{-1})	μ_e (D)
N_2	1.094[a]	–109.586[b]	9.902[a]	2.296[a]	0.
CO	1.1281[a]	–113.377[b]	11.242[c]	1.906[a]	0.118 (C^-O^+)[d]

[a] See reference [*7*].

[b] See reference [*16*].

[c] A. G. Gaydon, Dissociation Energies, revised edition (1953): D_e is corrected for zero-point energy.

[d] See references [*1, 18*].

the recent Hartree-Fock calculations with enlarged basis sets [*15, 9*] appear to be converging to a computed value of the dipole moment of CO equal in magnitude, but opposite in sign, to the accepted experimental value [*18, 1*]. Nesbet [*15*] pointed out, in a critical discussion of the experimental determination [*18*] of the polarity of the CO dipole moment, that the sign of the polarity has not in fact been established definitely by experiment.

In this paper, a perturbation theory of heteronuclear diatomic molecules based on the isoelectronic homonuclear molecules is developed. The heteronuclear molecule is regarded as the isoelectronic homonuclear molecule perturbed by a transfer of charge from one nucleus to the other. The situation is favorable for such an approach since the perturbation operator is simply a sum of one-electron terms. The molecular energy, equilibrium internuclear distance, dissociation energy, and electric dipole moment are considered in Section II. In Section III the Hartree-Fock approximations for calculating the effect of one-electron perturbations are briefly discussed. In Section IV the applicability of the perturbation theory is carefully considered and the theory is applied to the molecule CO based on N_2.

II. General Theory for Diatomic Molecules

1. *Molecular energy*

Let the heteronuclear molecule AB of interest have nuclear charges

$$Z_A = Z_0 (1 + \lambda) , \qquad (2.1)$$
$$Z_B = Z_0 (1 - \lambda) ,$$

and be taken to be the Z-perturbed condition of the isoelectronic homonuclear molecule CC with nuclear charges $Z_0 = (Z_A + Z_B)/2$. The electronic Hamiltonian of the Z-perturbed heteromolecule can be written

$$\mathscr{H} = \mathscr{H}_0 + \lambda V \qquad (2.2)$$

where $\mathscr{H}_0$ is the unperturbed electronic Hamiltonian and λ is the parameter

$$\lambda = (Z_A - Z_B)/(Z_A + Z_B) . \qquad (2.3)$$

The perturbation V is a sum of one-electron operators

$$V = \sum_{i=1}^{N} Z_0 \, (r_{Bi}^{-1} - r_{Ai}^{-1}) \qquad (2.4)$$

where r_{Ai} and r_{Bi} are the distances to the electron i from the nuclei A and B respectively. An important property of V is that it is antisymmetric with respect to inversion or interchange of nuclei A and B (u-symmetry).

The wavefunction Ψ for a particular nondegenerate electronic state and internuclear distance R of AB can be expanded in the familiar Rayleigh-Schrödinger power series in λ

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \mathcal{O}(\lambda^2)\,. \tag{2.5}$$

KATO [*11*] has proved that the series converges for a perturbation such as Eq. (2.4), at least for small enough λ. $\Psi^{(0)}$ is the wavefunction of the homonuclear molecule for the same electronic state (i.e., that which is adiabatically correlated by changing λ) and internuclear distance R. We shall take Ψ and $\Psi^{(0)}$ to be normalized so that $Re\,\langle \Psi^{(1)}, \Psi^{(0)} \rangle = 0$. The electronic energy expansion is

$$W = W^{(0)} + \lambda^2\, W^{(2)} + \mathcal{O}(\lambda^4) \tag{2.6}$$

where the terms in odd powers of λ vanish by symmetry*. $W^{(0)}$ is the electronic energy of the unperturbed homonuclear molecule, and the second-order energy coefficient $W^{(2)}$ is given by

$$W^{(2)} = \langle \Psi^{(0)}, V\,\Psi^{(1)} \rangle\,. \tag{2.7}$$

The molecular energy E of a diatomic molecule is the sum of the electronic energy W and the nuclear repulsion energy;

$$E(R) = W(R) + Z_A Z_B / R\,. \tag{2.8}$$

Hence by using Eqs. (2.1) and (2.6), we obtain

$$E - E^{(0)} = \lambda^2\,(W^{(2)} - Z_0^2/R) + \mathcal{O}(\lambda^4)\,. \tag{2.9}$$

Since $W^{(2)}$ must be negative for a ground state, it follows that the molecular energy E of the heteronuclear molecule must be lower than that of the homonuclear molecule $E^{(0)}$ at least for small λ.

2. Equilibrium internuclear distance

Let R_0 be the equilibrium internuclear distance for the homonuclear molecule CC; that is

$$\left(\frac{dE^{(0)}}{dR}\right)_0 \equiv \left(\frac{dE^{(0)}}{dR}\right)_{R=R_0} = 0\,. \tag{2.10}$$

Similarly let R_e be the equilibrium internuclear distance for the heteronuclear molecule AB; that is

$$\left(\frac{dE}{dR}\right)_e \equiv \left(\frac{dE}{dR}\right)_{R=R_e} = 0\,. \tag{2.11}$$

Differentiating Eq. (2.9) with respect to R we have

$$\frac{dE}{dR} - \frac{dE^{(0)}}{dR} = \lambda^2 \left(\frac{dW^{(2)}}{dR} + \frac{Z_0^2}{R^2}\right) + \mathcal{O}(\lambda^4)\,. \tag{2.12}$$

If we put $R = R_e$ and expand $dE^{(0)}/dR$ about R_0, we obtain

$$-(R_e - R_0)\left(\frac{d^2 E^{(0)}}{dR^2}\right)_0 + \cdots = \lambda^2 \left[\left(\frac{dW^{(2)}}{dR}\right)_e + \frac{Z_0^2}{R_e^2}\right] + \cdots\,, \tag{2.13a}$$

or

$$R_e - R_0 = -\frac{\lambda^2}{k_0}\left[\left(\frac{dW^{(2)}}{dR}\right)_e + \frac{Z_0^2}{R_e^2}\right] + \mathcal{O}(\lambda^4) \tag{2.13b}$$

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* This can be seen by observing that the energy must be invariant to an interchange of nuclei A and B, i.e., $\lambda \to -\lambda$.

where $k_0 = (d^2 E^{(0)}/dR^2)_0$ is the force-constant of the homonuclear molecule. Thus $R_e - R_0$ is of order λ^2, and the sign depends on the relative magnitude of the two terms in the square brackets; $dW^{(2)}/dR$ will be negative in general because $W^{(2)}$ is negative at $R = \infty$ and becomes zero at $R = 0$.

3. *Dissociation energy*

The dissociation energy of the heteronuclear molecule AB, D_e, and that of the homonuclear molecule, D_0, are given by

$$D_e = E(\infty) - E(R_e) \qquad (2.14)$$
$$D_0 = E^{(0)}(\infty) - E^{(0)}(R_0)\,.$$

Expanding $E(R_e)$ about R_0, we have

$$E(R_e) = E(R_0) + (R_e - R_0)\left(\frac{dE}{dR}\right)_0 + \cdots\,. \qquad (2.15)$$

Using Eqs. (2.12) and (2.13), we get

$$E(R_e) = E(R_0) + \mathcal{O}(\lambda^4)\,. \qquad (2.16)$$

Hence making use of Eqs. (2.9) and (2.16), we obtain

$$D_0 - D_e = \lambda^2 [\Delta W^{(2)}(R_0) - Z_0^2/R_0] + \mathcal{O}(\lambda^4) \qquad (2.17)$$

where

$$\Delta W^{(2)}(R_0) = W^{(2)}(R_0) - W^{(2)}(\infty)\,. \qquad (2.18)$$

Since $\Delta W^{(2)}(R_0) > 0$ in general, the sign of $D_0 - D_e$ depends on the relative magnitude of the two terms in Eq. (2.17).

4. *Electric dipole moment*

The dipole moment of the heteronuclear molecule AB is

$$\langle\mu\rangle = \langle\Psi, \mu\Psi\rangle = \langle\Psi^{(0)}, \mu\Psi^{(0)}\rangle + 2\lambda\langle\Psi^{(1)}, \mu\Psi^{(0)}\rangle + \mathcal{O}(\lambda^3) \qquad (2.19)$$

where A is taken to be on the z-axis at $R/2$ and B to be at $-R/2$, Ψ is assumed to be real for simplicity and

$$\mu = -\sum_{i=1}^{N} z_i + \lambda Z_0 R\,. \qquad (2.20)$$

The dipole moment expression can only contain odd powers of λ since it changes sign if λ changes sign. Hence, using Eq. (2.20), we get

$$\langle\mu\rangle = \lambda (Z_0 R + 2\langle\Psi^{(1)}, \mu\Psi^{(0)}\rangle) + \mathcal{O}(\lambda^3)\,; \qquad (2.21)$$

the dipole moment has been defined to be negative for $A^- B^+$.

The terms in Eq. (2.21) tend to cancel since $\langle\Psi^{(1)}, \mu\Psi^{(0)}\rangle$ is almost certainly negative. To see this consider the spectral expansion in terms of the unperturbed eigenfunctions $\Psi_n^{(0)}$:

$$\langle\Psi^{(1)}, \mu\Psi^{(0)}\rangle = \sum_{n\neq 0} \frac{V_{0n}\,\mu_{n0}}{E_0 - E_n}\,. \qquad (2.22)$$

The important point to notice is that both V and μ' ($= -\sum_i z_i$) have u-symmetry, and that $V\mu' \geq 0$ everywhere. This means that $V_{0n}\,\mu_{n0} \geq 0$ for the lower excited states, and could only be negative if the transition density ϱ_{n0} has different signs where V is the largest and where μ is the largest. This is only likely to occur for highly excited states, if at all. Since $E_0 - E_n < 0$, we conclude that $\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle$, the dipole due to the electronic charge shift caused by the Z-perturbation, is negative. This conclusion is supported by the Unsöld approximation for the sum in Eq. (2.22), which replaces the increasing denominators $E_0 - E_n$ by that of the smallest non-vanishing term, say $E_0 - E_1$;

$$\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle \simeq \frac{\langle \Psi^{(0)}, V \mu \, \Psi^{(0)} \rangle}{E_0 - E_1} . \tag{2.23}$$

This approximate expression is necessarily negative.

To decide the sign of $\langle \mu \rangle$ it is therefore necessary to perform an accurate calculation of the electronic term. It is interesting to note that by DALGARNO's interchange theorem [*4*, *8*] this can be written in the alternative form

$$\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle = \langle \chi^{(1)}, V \, \Psi^{(0)} \rangle \tag{2.24}$$

where $\chi^{(1)}$ is the solution of the equation

$$(\mathscr{H}_0 - E^{(0)}) \, \chi^{(1)} + (\mu - \lambda Z_0 \, R) \, \Psi^{(0)} = 0 . \tag{2.25}$$

Since both V and μ are one-electron operators the interchanged form does not possess any obvious advantage.

5. *Schwartz discriminant*

A simple check on the validity of merely taking the leading terms in the power series for $W - W^{(0)}$ in Eq. (2.6) and for $\langle \mu \rangle$ in Eq. (2.21) is provided by the Schwartz-like inequality

$$\sum_{n \neq 0} \frac{V_{n0}^2}{E_0 - E_n} \sum_{n \neq 0} \frac{\mu_{n0}^2}{E_0 - E_n} \geq \left(\sum_{n \neq 0} \frac{V_{0n} \, \mu_{n0}}{E_0 - E_n} \right)^2 . \tag{2.26}$$

Using Eqs. (2.6), (2.21) and (2.22), we obtain

$$\left(\frac{W^{(0)} - W}{\lambda^2} \right) \left(\frac{\alpha}{2} \right) \geq \left(\frac{\lambda \, Z_0 \, R - \langle \mu \rangle}{2 \, \lambda} \right)^2 \tag{2.27a}$$

or

$$W^{(0)} - W \geq \frac{(\lambda \, Z_0 \, R - \langle \mu \rangle)^2}{2 \, \alpha} \tag{2.27b}$$

where α is the polarizability of the homonuclear molecule parallel to the axis, given by

$$\alpha = -2 \sum_{n \neq 0} \frac{\mu_{0n}^2}{E_0 - E_n} . \tag{2.28}$$

This inequality is checked below for the case of CO and N_2.

III. The Hartree-Fock Approximation

In this section the calculation of the effect of a one-electron perturbation on an atomic or a molecular system is discussed. It has already been pointed out that the perturbation V [Eq. (2.4)] is a sum of one-electron terms. Since a comprehensive review paper on the calculation of the effect of one-electron perturbations on atoms has recently appeared [*3*] the uncoupled Hartree-Fock approximation [*2*, *10*] alone will be briefly discussed.

The uncoupled Hartree-Fock approximation

The difficulty in solving the equations for the first-order wavefunctions in the coupled Hartree-Fock approximation [*3*] is due to the coupling terms which arise from the demand for self-consistency in the presence of the perturbation V. A simpler set of equations for the first-order wavefunction can be obtained by neglecting the effect of the perturbation on the Hartree-Fock potential. The perturbed equation for this so-called uncoupled Hartree-Fock approximation is then

$$(H_0 + \lambda V - W)\,\Psi = 0 \tag{3.1}$$

where H_0 is the Hartree-Fock Hamiltonian for the unperturbed system. By expanding Eq. (3.1) in powers of λ, we obtain the set

$$(H_0 - W^{(0)})\,\Psi^{(0)} = 0 \tag{3.2}$$

$$(H_0 - W^{(0)})\,\Psi^{(1)} + (V - W^{(1)})\,\Psi^{(0)} = 0\,. \tag{3.3}$$

Because of its one-electron character, V can be written in the form,

$$V = \sum_i v\,(i) \tag{3.4}$$

and the first-order wavefunction $\Psi^{(1)}$ can be written as

$$\Psi^{(1)} = \sum_{i=1}^{N} \mathscr{A} \prod_{j \neq i}^{N} \varphi_j^{(0)}\,(j)\,\varphi_i^{(1)}\,(i) \tag{3.5}$$

where $\mathscr{A}$ is the antisymmetrizing operator and $\varphi_i^{(1)}\,(i)$ is the first-order perturbation correction to $\varphi_i^{(0)}\,(i)$. Eq. (3.3) then separates into a set of uncoupled one-electron equations

$$\begin{aligned}&(F\,(i) - w_i^{(0)})\,\varphi_i^{(1)} + (v\,(i) - w_i^{(1)})\,\varphi_i^{(0)} \\ &= \sum_{j \neq i}^{N} \{(w_j^{(0)} - w_i^{(0)})\,\langle \varphi_j^{(0)}, \varphi_i^{(1)} \rangle + \langle \varphi_j^{(0)}, v\,\varphi_i^{(0)} \rangle\}\,\varphi_j^{(0)}\,,\end{aligned} \tag{3.6}$$

where $F\,(i)$ is the unperturbed one-electron Hartree-Fock operator for electron i, $w_i^{(0)}$ is the unperturbed Hartree-Fock orbital energy and $w_i^{(1)}$ is the first-order orbital energy.

A variational approximation to the solution of Eq. (3.6) can be obtained by minimizing the functional

$$\begin{aligned}\widetilde{w}_i^{(2)} = {} & \langle \widetilde{\varphi}_i^{(1)}, (F - w_i^{(0)})\,\widetilde{\varphi}_i^{(1)} \rangle + \langle \widetilde{\varphi}_i^{(1)}, (v - w_i^{(1)})\,\varphi_i^{(0)} \rangle + \\ & + \langle \varphi_i^{(0)}, (v - w_i^{(1)})\,\widetilde{\varphi}_i^{(1)} \rangle - \sum_{j \neq i}^{N} \{(w_j^{(0)} - w_i^{(0)}) |\, \langle \widetilde{\varphi}_i^{(1)}, \varphi_j^{(0)} \rangle\,|^2 + \\ & + \langle \widetilde{\varphi}_i^{(1)}, \varphi_j^{(0)} \rangle\,\langle \varphi_j^{(0)}, v\,\varphi_i^{(0)} \rangle + \langle \varphi_i^{(0)}, v\,\varphi_j^{(0)} \rangle\,\langle \varphi_j^{(0)}, \widetilde{\varphi}_i^{(1)} \rangle\}\,.\end{aligned} \tag{3.7}$$

If we substitute

$$\widetilde{\varphi}_i^{(1)} = \varphi_i^{(0)}\,\widetilde{f}_i \tag{3.8}$$

into Eq. (3.7) and neglect the contribution from the nonlocal potential of $F\,(i)$ in the first term in Eq. (3.7) [*10*] we obtain

$$\begin{aligned}\widetilde{w}_i^{(2)} = {} & \tfrac{1}{2}\,\langle \varphi_i^{(0)}, |\,\nabla\,\widetilde{f}_i\,|^2\,\varphi_i^{(0)} \rangle + \langle \varphi_i^{(0)}, (v - w_i^{(1)})\,(\widetilde{f}_i^* + f_i)\,\varphi_i^{(0)} \rangle - \\ & - \sum_{j \neq i}^{N} \{(w_j^{(0)} - w_i^{(0)})\,|\,\langle \varphi_i^{(0)}, \widetilde{f}_i^*\,\varphi_j^{(0)} \rangle\,|^2 + \\ & + \langle \varphi_i^{(0)}, (\widetilde{f}_i^* + \widetilde{f}_i)\,\varphi_j^{(0)} \rangle\,\langle \varphi_j^{(0)}, v\,\varphi_j^{(0)} \rangle\}\,.\end{aligned} \tag{3.9}$$

This equation only involves one-electron integrals and will be used in the following section.

IV. Treatment of CO Based on N_2

1. Electronic potential energy curves

Let $\Psi_1^{(0)}$ and $W_1^{(0)}$ be the wave function and the electronic energy for the lowest ${}^1\sum_g^+$ state of N_2 which dissociates to N atoms in ground ${}^4S$ states, and $\Psi_2^{(0)}$ and $W_2^{(0)}$ be those for the ${}^1\sum_g^+$ state of N_2 which dissociates to the ions, N^+ and N^-, in ground ${}^3P$ states. Then using the ionization potential [*14*] and electron affinity [*5*] of the N atom, we obtain

$$\begin{aligned} W_2^{(0)}(\infty) - W_1^{(0)}(\infty) &= (\text{I.P. of N}) - (\text{E. A. of N}) \\ &= (14.54 - 0.05)\ \text{eV} \qquad (4.1) \\ &= 14.49\ \text{eV} \\ &= 0.5325\ \text{H}\,. \end{aligned}$$

Similarly let Ψ_1 and W_1 be the wave function and the electronic energy of the lowest ${}^1\sum^+$ state of CO which dissociates to atoms C and O in ${}^3P$ states, and Ψ_2 and W_2 be those for the ${}^1\sum^+$ state which dissociates to ions C^- and O^+ in ${}^4S$ states. Then using the ionization potential [*14*] of the O atom, and the electron affinity [*5*] of the C atom we obtain

$$\begin{aligned} W_2(\infty) - W_1(\infty) &= (\text{I. P. of O}) - (\text{E. A. of C}) \\ &= (13.61 - 1.12)\ \text{eV} \qquad (4.2) \\ &= 12.49\ \text{eV} \\ &= 0.4590\ \text{H}\,. \end{aligned}$$

From the electronic energies of N, C^- and O^+ which are computed from ionization potentials [*14*] the energy difference of $2\,N - (C^- + O^+)$ is

$$\begin{aligned} W_1^{(0)}(\infty) - W_2(\infty) &= \{(\text{I. Ps. of } O^+) + (\text{I. Ps. of C}) + (\text{E. A. of C})\} - 2\,(\text{I.Ps. of N}) \\ &= \{2029.66 + 1029.81 + 1.12\} - 2 \times 1485.65\ \text{eV} \\ &= 89.29\ \text{eV} \qquad (4.3) \\ &= 3.281\ \text{H}\,. \end{aligned}$$

This is to be compared with the value calculated by Eq. (A.6) in the Appendix

$$W_1^{(0)}(\infty) - W_2(\infty) \simeq \sum_{i=1}^{7} \frac{1}{n_i^2} = 3.250\ \text{H} \qquad (4.4)$$

which agrees well with the empirical value [Eq. (4.3)].

The energy difference between C + O atoms and N + N atoms (ground states) has been calculated using the $1/Z$-expansion through the first-order. The result, $W_1^{(0)}(\infty) - W_1(\infty) \simeq 2.85$ H, is to be compared with the empirical value, 3.74 H, computed using the ionization potential [*14*] of each electron of N, C and O atoms. The poor agreement shows that higher order terms should be included in the $1/Z$-expansions of the electronic energies of the atoms.

The electronic energies as functions of the internuclear separation R are shown schematically as in Fig. 1.

2. Schwartz discriminant

The object of this section is to check the inequality Eq. (2.27b). To find $\Delta W(R_0) = W_1(R_0) - W_1^{(0)}(R_0)$ where R_0 is the equilibrium internuclear distance of N_2, we expand the molecular energy of CO, $E_1(R)$, which is the sum of the electronic energy and the internuclear repulsion energy, about the equilibrium internuclear distance, R_e

$$E_1(R) = E_1(R_e) + \tfrac{1}{2}(R - R_e)^2 \left(\frac{d^2 E_1}{d R^2}\right)_e + \cdots \tag{4.5}$$

where $(d^2 E_1/dR^2)_e = k_e$ is the force constant for CO. Also we note that

$$\begin{aligned} E_1^{(0)}(R_0) &= -D_1^{(0)} + E_1^{(0)}(\infty) \\ E_1(R_e) &= -D_1 + E_1(\infty) \end{aligned} \tag{4.6}$$

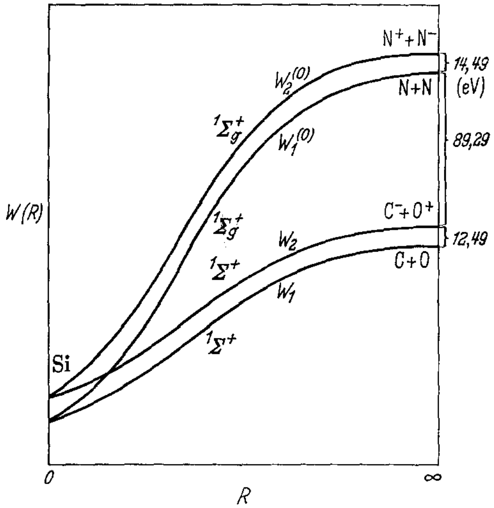


Fig. 1. Schematic plot of the empirical electronic energy $W(R)$ against the internuclear separation R for relevant states of CO and N_2

where $D_1^{(0)}$ and D_1 are the dissociation energies of N_2 and CO. Using Eqs. (4.5) and (4.6), we obtain

$$\begin{aligned} -\Delta W(R_0) \simeq{}& (D_1 - D_1^{(0)}) + \{E_1^{(0)}(\infty) - E_1(\infty)\} + \\ &+ (Z_c Z_0 - Z_N^2)/R_0 - (R_0 - R_e)^2 k_e/2 \end{aligned} \tag{4.7}$$

where Z_N, Z_C and Z_O are the nuclear charges of N, C and O. By making use of the necessary molecular constants given in Tab. 1, we obtain

$$\Delta W(R_0) \approx -3.3\ \mathrm{H}. \tag{4.8}$$

Since $\langle\mu\rangle = -0.15$ Debye [9] and $\alpha = 23.8 \times 10^{-25}\ \mathrm{cm}^3$ [13], we get

$$(\lambda Z_N R_0 - \langle\mu\rangle)^2/(2\alpha) \approx 0.13\ \mathrm{H}. \tag{4.9}$$

The inequality (2.27b) becomes $3.3 \geq 0.13$, and is thus easily satisfied for the case of N_2 and CO. The use of the leading terms in the perturbation expansions is therefore not in conflict with the Schwartz inequality.

3. *Correlation of the electronic states and degeneracy*

The proposed perturbation treatment in Section II expands the wavefunction Ψ_1 and energy $W_1(R)$ for the lowest state of CO about those for the lowest state of N_2, namely $\Psi_1^{(0)}$ and $W_1^{(0)}(R)$, in powers of $\lambda = (Z_A - Z_B)/(Z_A + Z_B)$. The expansions are given in Eqs. (2.5) and (2.6). However, the treatment in Section II overlooks the following difficulty: the electronic states of CO and N_2 which are related by the perturbation theory must be "adiabatically correlated" in the sense that if λ were reduced from $\frac{1}{7}$ to 0 the states must become identical.

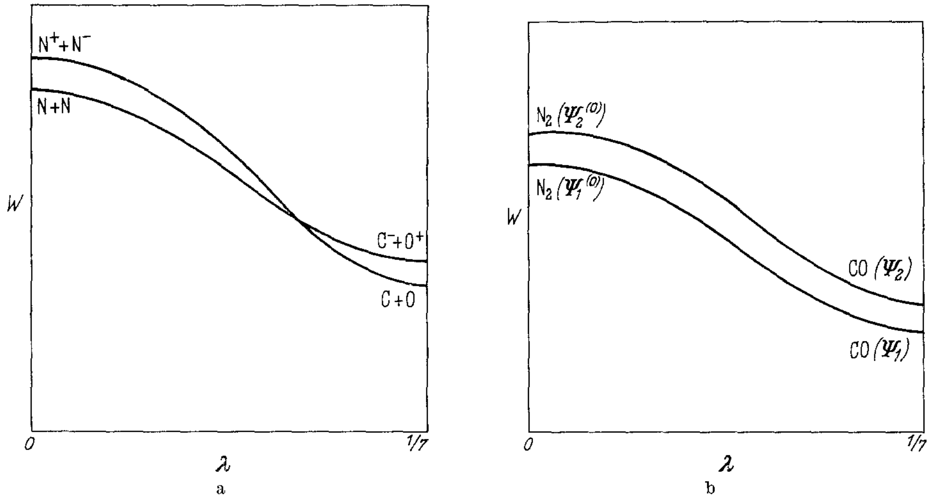
When the atoms are separated at $R = \infty$ we know that in fact the state C + O is correlated with $N^+ + N^-$, and the state N + N is correlated with $C^- + O^+$. That is:

$$\lim_{\lambda\to 0}\lim_{R\to\infty} \Psi_1 = \Psi_2^{(0)} \tag{4.10}$$

although

$$\lim_{\substack{\lambda\to 0\\(R\approx R_0)}} \Psi_1 = \Psi_1^{(0)} . \tag{4.11}$$

When $R = 0$ at the united atom (Si) the energies are independent of λ since the nuclei are united, and only the total charge Z (= 14) matters. The correlations of the states are shown schematically in Fig. 2.



a b

Fig. 2. Correlation of the electronic states. a) $R = \infty$, b) $R \approx R_0$

To check the applicability of the proposed perturbation theory, we consider the crossing point of the two states. At the limit as $R \to \infty$, the separated ions N^+ and N^- are in different ground ^3P states and there exist four degenerate $^1\Sigma^+$ states [7] which are coupled by the perturbation V. Hence degenerate perturbation theory must be applied. Suppose that the four $^1\Sigma^+$ states of $N^+ + N^-$ can be described by the orthonormal wave functions $\varphi_1(a, b)$, $\varphi_1(b, a)$, $\varphi_2(a, b)$ and $\varphi_2(b, a)$ where $\varphi_1(b, a)$ and $\varphi_2(b, a)$ are obtained from $\varphi_1(a, b)$ and $\varphi_2(a, b)$ by interchanging nitrogen nuclei A and B. From these four wave functions, we can construct two symmetric wave functions and two antisymmetric wave functions;

$$\begin{aligned}
\psi_{1g} &= \frac{1}{\sqrt{2}}\{\varphi_1(a, b) + \varphi_1(b, a)\}\\
\psi_{2g} &= \frac{1}{\sqrt{2}}\{\varphi_2(a, b) + \varphi_2(b, a)\}\\
\psi_{3u} &= \frac{1}{\sqrt{2}}\{\varphi_1(a, b) - \varphi_1(b, a)\}\\
\psi_{4u} &= \frac{1}{\sqrt{2}}\{\varphi_2(a, b) - \varphi_2(b, a)\} .
\end{aligned} \tag{4.12}$$

Since the perturbation V has u-symmetry the secular equation is given by

$$\begin{vmatrix} -W^{(1)} & 0 & V_{13} & V_{14} \\ 0 & -W^{(1)} & V_{23} & V_{24} \\ V_{31} & V_{32} & -W^{(1)} & 0 \\ V_{41} & V_{42} & 0 & -W^{(1)} \end{vmatrix} = 0 \tag{4.13}$$

where $V_{ij} = \langle \psi_i, V \psi_j \rangle$. By solving Eq. (4.13) we can obtain the lowest first-order energy $W_2^{(1)}$.

On the other hand, the separated atoms N + N are in the same ^4S state at the limit as $R \to \infty$, and can be treated as a non-degenerate case since only one $^1\sum_g^+$ state exists. Hence in general we shall have

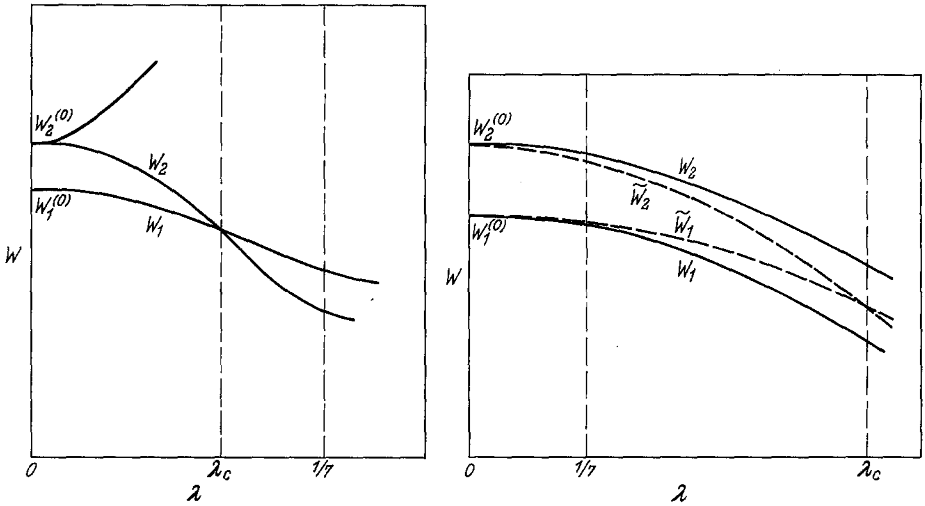
$$W_1(\infty) = W_1^{(0)}(\infty) + \lambda^2 W_1^{(2)}(\infty) + \cdots, \tag{4.14a}$$

$$W_2(\infty) = W_2^{(0)}(\infty) + \lambda W_2^{(1)}(\infty) + \cdots. \tag{4.14b}$$

Therefore the approximate crossing point at $R = \infty$ is

$$\lambda_c(R = \infty) \simeq -\frac{\Delta W^{(0)}(\infty)}{W_2^{(1)}(\infty)} \tag{4.15}$$

Since the denominator in Eq. (4.15) is the first order energy coefficient, λ_c $(R = \infty)$ may be smaller than $\frac{1}{7}$, (see Fig. 3a).



a b

Fig. 3. Schematic plot of the electronic energy W against the perturbation parameter λ. $\tilde{W}_1$ and $\tilde{W}_2$ are given by Eqs. (4.18a) and (4.18b). a) $R = \infty$, b) $R \approx R_0$

When R is near the equilibrium internuclear separation of N_2, R_0, we approximate the two states of CO as follows:

$$\tilde{\Psi}_1 = \Psi_1^{(0)} + \lambda \Psi_1^{(1)}$$

$$\tilde{\Psi}_2 = \Psi_2^{(0)} + \lambda \Psi_2^{(1)} \tag{4.16}$$

where $\Psi_1^{(1)}$ and $\Psi_2^{(1)}$ are the solutions of the first-order perturbation equations

$$(\mathscr{H}_0 - W_i^{(0)}) \Psi_i^{(1)} + V \Psi_i^{(0)} = 0, \quad i = 1, 2. \tag{4.17}$$

Then since $W_1^{(1)} = W_2^{(1)} = 0$ and $W_1^{(3)} = W_2^{(3)} = 0$ due to u-symmetry of V, we have

$$\tilde{W}_1 = W_1^{(0)} + \frac{\lambda_2 W_1^{(2)}}{1 + \lambda^2 S_1} \tag{4.18a}$$

$$\tilde{W}_2 = W_2^{(0)} + \frac{\lambda^2 W_2^{(2)}}{1 + \lambda^2 S_2} \tag{4.18b}$$

where $S_1 = \langle \Psi_1^{(1)}, \Psi_1^{(1)} \rangle$ and $S_2 = \langle \Psi_2^{(1)}, \Psi_2^{(1)} \rangle$. If we put $\tilde{W}_1 = \tilde{W}_2$ and neglect λ^2 terms in denominators, we obtain the approximate crossing point

$$\lambda_c = \sqrt{-\frac{\Delta W^{(0)}}{\Delta W^{(2)}}} \tag{4.19}$$

where $\Delta W^{(0)} = W_2^{(0)} - W_1^{(0)}$ and $\Delta W^{(2)} = W_2^{(2)} - W_1^{(2)}$. Note that λ_c is real only if $\Delta W^{(0)} \, \Delta W^{(2)} < 0$, which is in fact the case. Since it appears that $|\Delta W^{(0)}| \gg |\Delta W^{(2)}|$ (see Fig. 3b), we assume that $\lambda_c \gg \frac{1}{7}$.

Hence we conclude that the proposed perturbation theory may be applied when R is not too large.

4. Calculation of second-order energy and dipole moment

Variational solutions of the first-order Eq. (3.6) have been obtained by means of Eq. (3.9), and used to calculate the second-order energy and dipole moment. Two sets of approximate Hartree-Fock molecular orbitals for N_2 were employed: 1. NESBET's molecular wavefunctions [*15*] and 2. RANSIL's best limited LCAO-MO [*17*]. For the functions $\tilde{f}_i$, four- and seven-term polynomials were employed:

$$\tilde{f}_{i\alpha} = -\frac{4 Z_0}{R} (a_{i1} \eta + a_{i2} \xi\eta + a_{i3} \xi^2 \eta + a_{i4} \eta^3) \tag{4.20a}$$

and

$$\tilde{f}_{i\beta} = \tilde{f}_{i\alpha} - \frac{4 Z_0}{R} (a_{i5} \xi\eta^3 + a_{i6} \xi^2 \eta^3 + a_{i7} \eta^5) \tag{4.20b}$$

where ξ and η are prolate spheroidal coordinates defined by

$$\xi = \frac{r_A + r_B}{R}\,; \quad \eta = \frac{r_A - r_B}{R}\,. \tag{4.21}$$

The variational coefficients a_{ij}, in Eqs. (4.20a) and (4.20b) were determined by minimizing the functional (3.9).

It should be noticed that the operators v and μ have u-symmetry, and therefore the functions $\tilde{f}_i$ should also have u-symmetry. Hence the integrals $\langle \psi_i, v\, \psi_j \rangle$ and $\langle \psi_i, \mu\, \psi_j \rangle$ vanish unless the spatial functions ψ_i and ψ_j have different inversion symmetry. Furthermore, the required molecular integrals

$$\langle \chi, \frac{\xi^m \eta^n}{\xi^2 - \eta^2} \chi' \rangle$$

and

$$\langle \chi, \xi^m \eta^n \chi' \rangle$$

where χ and χ' are Slater-type AO's centered at atom A or B, are easily expressed in terms of the auxiliary functions

$$A_m(t) = \int_1^\infty e^{-t\xi} \xi^m \, d\xi$$

$$B_n(t) = \int_{-1}^{+1} e^{-t\eta} \eta^n \, d\eta \,. \tag{4.22}$$

Table 2. *Calculated energy* (Hartrees) *and dipole moment* (a. u.) of CO

R (B)		1.868^c	2.068^c	2.268^c	2.068^d
$E^{(0)}$		–108.94320	–108.97143	–108.92938	–108.63359
$\lambda^2 W^{(2)}$	a	– 5.833	– 6.727	– 7.889	– 6.724
	b	– 5.877	– 6.776	– 7.952	– 6.789
$-1/R$		– 0.535	– 0.484	– 0.441	– 0.484
E	a	–115.311	–116.182	–117.259	–115.842
	b	–115.355	–116.231	–117.322	–115.907
$\langle\mu\rangle^e$	a	– 5.966	– 9.436	– 14.363	– 12.607
	b	– 6.064	– 9.562	– 14.554	– 12.767

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[a] Four-term perturbation polynomial was used [Eq. (4.20a)].

[b] Seven-term perturbation polynomial was used [Eq. (4.20b)].

[c] NESBET's [*15*] molecular wavefunction for N_2 was used.

[d] RANSIL's best limited LCAO–MO [*17*] was used.

[e] Dipole moment was defined as negative for $C^+ O^-$. (See Section II.4).

Table 3. *Energy* (Hartrees) *and dipole moment* (a.u.) *of* NESBET's [*15*] *molecular wavefunction for* CO

R (B)	1.808393	1.932	2.132	2.323	2.455607
E	–112.66220	–112.72952	–112.75878	–112.73211	–112.70106
$\langle\mu\rangle$	0.0830	– 0.0032	– 0.1562	– 0.3246	– 0.4342

Table 4. *Expansion coefficients in the perturbation polynomial and orbital contributions to the second-order energy and dipole moment for* $R = 2.068$. *Zeroth-order wavefunction is* NESBET's [*15*] *molecular wavefunction for* N_2

Coefficients in $\tilde{f}_{i\alpha}$ [four-term perturbation polynomial, Eq. (4.20a)]

Orbital	a_{i1}	a_{i2}	a_{i3}	a_{i4}	$w_i^{(0)}$ (H)	$\lambda^2 w_i^{(2)}$ (H)	$\lambda\mu_i^{(1)}$ (a.u.)
$1\sigma_g$	–1.2346	0.5160	0.0296	0.0367	–15.69623	–0.4875	–0.0020
$2\sigma_g$	–0.8774	0.1152	0.0406	0.1250	– 1.48569	–0.3250	–0.1279
$3\sigma_g$	–1.0078	0.3561	–0.0131	–0.0291	– 0.64278	–0.2378	–0.0511
$1\sigma_u$	–1.1463	0.5007	0.0369	0.0043	–15.69262	–0.4721	+0.0008
$2\sigma_u$	–1.0249	0.3575	–0.0042	–0.0445	– 0.78581	–0.2257	+0.0771
$1\pi_u$	–1.7743	0.1897	–0.0250	0.4672	– 0.62261	–0.8078	–1.3864

The calculated results of the second-order energy, molecular energy and dipole moment are given in Tab. 2. To compare the present results with those of a direct Hartree-Fock calculation, the molecular energy and dipole moment of NESBET's [*15*] molecular wavefunction for CO are shown in Tab. 3. To further show the dependence of the second-order energy and dipole moment on the choice of trial functions $\tilde{f}_i$, the coefficients in the four-term perturbation polynomials [Eq. (4.20a)], and also the orbital contributions to the second-order energy and dipole moment, are given in Tab. 4.

The results for $R = 2.068$ B using RANSIL's [*17*] and NESBET's [*15*] molecular wavefunctions for N_2 as zeroth-order wavefunction show that the molecular properties in this calculation are not very sensitive to the choice of zeroth-order wavefunction (see Tab. 2).

The calculated molecular energy of CO is too low by $2.0 \sim 6.0$ H in the given range of R and decreases too fast as R becomes larger. (See Tab. 2 and 3). Hence the calculated molecular energy does not give a minimum in the range of R investigated as implied by Eq. (2.12).

The calculated dipole moment of CO is ridiculously large in magnitude compared with the results of Hartree-Fock calculations [*15, 9*] and the experimental value [*1*]. The large magnitude of the dipole moment is mainly due to the abnormally large contribution from the $1\,\pi_u$ orbital.

V. Discussion

The present quantitative results of this theory for the isoelectronic molecules N_2 and CO are disappointing. The calculated molecular energy of CO is too low and does not give a minimum in the given range of internuclear separation R. It is shown, however, that the polarity of the electric dipole moment of CO agrees with the results of recent Hartree-Fock calculations [*15, 9*] at the equilibrium separation, although the magnitude is too large. It should be noticed that the SCF–LCAO–MO approximation to the Hartree-Fock solution of N_2 was employed for zeroth-order wavefunction, and the uncoupled Hartree-Fock approximation was used to determine the second-order energy and the first-order wavefunction. The use of the coupled Hartree-Fock approximation might improve the result.

It is interesting to note that the molecular energy difference $\Delta E = E_{\mathrm{CO}} - E_{\mathrm{N_2}}$ may be obtained directly by means of the integral Hellmann-Feynman theorem formulated by Kim and Parr [*12*]. In this case the theorem takes the form

$$\Delta E = -\lambda^2 Z_0^2/R + \frac{\langle \Psi_{\mathrm{CO}}, \lambda V \Psi_{\mathrm{N_2}} \rangle}{\langle \Psi_{\mathrm{CO}}, \Psi_{\mathrm{N_2}} \rangle} \tag{5.1}$$

where the first term is the nuclear-nuclear repulsion energy difference and Ψ_{CO} and $\Psi_{\mathrm{N_2}}$ may be approximated by Hartree-Fock wavefunctions for CO and N_2. The advantage of Eq. (5.1) is that it is valid whether or not λV is small. If the right hand side of Eq. (5.1) is expanded in powers of λ, it reduces to the perturbation series, Eq. (2.9).

A related perturbation treatment for acetylene based on the isoelectronic molecule N_2 has been performed by Gilson and Arents [*6*]. However, in this case the first-order energy does not vanish, and it alone was calculated. The error involved was about twice that in the present paper, but in the opposite direction.

The significance of the present theory is that it provides a method of comparing the properties of iso-electronic molecules by a perturbation procedure. The perturbation operator [see Eq. (2.4)] has u-symmetry and is a sum of one-electron operators. The symmetry feature of the perturbation operator simplifies the actual calculation of the energy and other molecular properties for diatomic molecules, as shown in Section IV, 4. The one-electron character of this operator allows the use of the well-developed theory of the one-electron perturbation effect. (Cf. Section III.)

The theory might be extended to polyatomic molecules and crystals. For example, borazine, $B_3N_3H_6$, might be treated with benzene, C_6H_6, as the unperturbed system, and borazon, $(BN)_\infty$, with diamond as the unperturbed system. For these cases, $\lambda = (Z_{\mathrm{N}} - Z_{\mathrm{B}})/(Z_{\mathrm{N}} + Z_{\mathrm{B}}) = \frac{1}{6}$. On the other hand, the diatomic molecule BF, with N_2 as the unperturbed system, would have $\lambda = \frac{2}{7}$ which is probably too large for the theory to work.

Acknowledgements. The authors would like to thank Dr. T. H. WALNUT for correcting an elementary but vital error in the original treatment. We are also very grateful to Dr. S. T. EPSTEIN for numerous invaluable discussions about the Hartree-Fock approximations, and to Dr. J. O. HIRSCHFELDER for helping to clarify the behavior of the energy curves in the presence of degeneracy. Thanks are also due to Mr. H. v. HIRSCHHAUSEN for a critical reading of the manuscript, which has led to many improvements in presentation.

Appendix

Energy difference for separated atoms

The electronic energy difference at the infinite internuclear separation, $[W(\infty) - W^{(0)}(\infty)]$, can be easily computed using the $1/Z$-expansion for the atomic energies. For an atom with nuclear charge Z_0 and N electrons, the electronic energy can be expanded as follows

$$\mathscr{E}(Z_0, N) = Z_0^2\,\varepsilon^{(0)}(N) + Z_0\,\varepsilon^{(1)}(N) + \varepsilon^{(2)}(N) + \varepsilon^{(3)}(N)/Z_0 + \mathscr{O}(1/Z_0^2)\,. \tag{A.1}$$

For the perturbed condition, that is, an atom with nuclear charge $Z_0(1+\lambda)$ and an atom with nuclear charge $Z_0(1-\lambda)$, the total energy is

$$\begin{aligned} W(\infty) &= \mathscr{E}[Z_0(1+\lambda), N] + \mathscr{E}[Z_0(1-\lambda), N] \\ &= 2\{Z_0^2\,\varepsilon^{(0)}(N) + Z_0\,\varepsilon^{(1)}(N) + \varepsilon^{(2)}(N) + \varepsilon^{(3)}(N)/Z_0 + \cdots\} + \\ &\quad + 2\lambda^2\{Z_0^2\,\varepsilon^{(0)}(N) + \varepsilon^{(3)}(N)/Z_0 + \cdots\} + 2\lambda^4\{\varepsilon^{(3)}(N)/Z_0 + \cdots\}\,. \end{aligned} \tag{A.2}$$

Since $W^{(0)}(\infty) = 2\,\mathscr{E}(Z_0, N)$, the energy difference is given by

$$W(\infty) - W^{(0)}(\infty) = 2\lambda^2\{Z_0^2\,\varepsilon^{(0)}(N) + \varepsilon^{(3)}(N)/Z_0 + \cdots\} + \mathscr{O}(\lambda^4)\,. \tag{A.3}$$

Hence we obtain

$$W^{(2)}(\infty) = 2\{Z_0^2\,\varepsilon^{(0)}(N) + \varepsilon^{(3)}(N)/Z_0 + \mathscr{O}(1/Z_0^2)\}\,. \tag{A.4}$$

The interesting feature is that $W^{(2)}(\infty)$ contains neither the average repulsion term $\varepsilon^{(1)}(N)$ nor the second order term $\varepsilon^{(2)}(N)$. The third order term $\varepsilon^{(3)}(N)$ is expected to be very much smaller than $\varepsilon^{(0)}(N)$. If the ith electron in a hydrogenic orbital has principal quantum number n_i, then

$$\varepsilon^{(0)}(N) = -\tfrac{1}{2}\sum_{i=1}^{N}\frac{1}{n_i^2}\,. \tag{A.5}$$

Note that if $Z_A = Z_0 + 1$ and $Z_B = Z_0 - 1$, so that $\lambda Z_0 = 1$, then

$$\mathscr{E}(Z_A, N) + \mathscr{E}(Z_B, N) - 2\,\mathscr{E}(Z_0, N) \simeq -\sum_{i=1}^{N}\frac{1}{n_i^2}\,. \tag{A.6}$$

This corresponds to the energy difference between the ion pair $A^+ + B^-$ and two neutral atoms, C, each having N electrons.

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(Received December 2, 1965)