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LONG-RANGE ATOMIC INTERACTION POTENTIALS FOR NITROGEN

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16. Abstract

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SUMMARY

Direct correlations between molecular and atomic wave functions are employed to find the coefficients of the two-electron exchange energies in the valence-bond description of the interatomic forces between colliding nitrogen atoms. Whereas the X $^1\Sigma_g^+$ and $^7\Sigma_u^+$ potentials are identical with those deduced previously, the A $^3\Sigma_u^+$ and $^5\Sigma_g^+$ potentials are very different. Not only are the long-range tails of the second pair revealed as mirror images of each other, as are the first two, but also each is expressed as a simple fraction of the lowest curve. A more general discussion of the different types of diatomic bonds and antibonds, including comparisons with those of the current literature, also is presented.

INTRODUCTION

The long-range tails of interatomic potentials are important for many calculations of the nonequilibrium properties of collision-dominated gases. Often used for this purpose is the approximation of perfect pairing (ref. 1), hereafter called APP, in which molecular energies are expressed as linear combinations of bond and antibond energies based upon symmetry and spin pairing considerations. Although the absolute results for individual collisions may be inaccurate, the method is thought to establish fairly reliable and useful relations between the various potentials operating in a gas. (See ref. 2 for a discussion.) Hence, if a small number of such potentials can be computed accurately (see refs. 3 to 5 for ab initio quantum mechanical calculations of the N_2 ground state), the others will follow from simple APP theory.

A principal objective of the present research is to supply the APP bond and antibond energies for collisions between two ground-state nitrogen atoms and corresponding to molecular electron configurations determined from correlation studies similar to that of Mulliken (ref. 6) for the $N_2\left(^5\Sigma_g^+\right)$ state. More general APP multielectron energies also are considered and several important relations are discussed. The correlation analysis forces the molecule to separate into atoms with the desired spin and angular momentum quantum numbers, a requirement which has not always been satisfied in previous calculations. Vanderslice, Mason, and Lippincott (ref. 7), for example, assume that of the several different electron configurations which correspond to a given set of molecular quantum numbers, only the strongest attractive or the least repulsive one dissociates into normal atoms. Such assumptions are seldom valid and frequently yield incorrect results for the interaction potentials.

The long-range potential tails thus computed for the $N_2\left(X\ ^1\Sigma_g^+\right)$, $N_2\left(A\ ^3\Sigma_u^+\right)$, $N_2\left(^5\Sigma_g^+\right)$, and $N_2\left(^7\Sigma_u^+\right)$ states are compared with each other and with Gilmore's extrapolations (ref. 8) of Rydberg-Klein-Rees (designated "RKR") data. Although the latter curves are somewhat uncertain in the region of interest, a pronounced preference is shown for the present calculations over those of reference 7 mentioned previously. In addition, the present theory yields much simpler relations between the energies than does reference 7 because each of the three excited potentials can be expressed for the first time directly in terms of the molecular ground-state energy. Vanderslice, Mason, and Lippincott, on the other hand, are left with two independent potentials, one of which they obtain by a delta-function computation of $N_2\left(^7\Sigma_u^+\right)$ and the other by a rather questionable analysis of predissociation data. The latter procedure is unnecessary in the present refinement.

SYMBOLS

a,b	atoms a and b; reference to nuclei when used as subscripts; atomic functions
C_1, C_2, C_3	variational coefficients in equation (18)
e	absolute electron charge
E_0	ground-state energy of atomic hydrogen
E(He)	ground-state energy of atomic helium
F	arbitrary operator in equation (C1)
H	Hamiltonian operator
$I, \bar{I}$	atomic functions, $p_x + ip_y$ and $p_x - ip_y$
i,j	integers

J_i	exchange energy for an i-electron bond; subscripts σ or π refer to $i = 2$
L	quantum number for total orbital angular momentum
L_{max}	maximum value of L
L_+, L_-	step-up, step-down or ladder operators
M_L	magnetic quantum number for total orbital angular momentum
M_S	magnetic quantum number for total spin
O	atomic function p_z
O_L	projection operator
p_x, p_y, p_z	p-type atomic orbitals
Q_i	Coulomb energy for an i-electron bond
r	ratio defined by equation (31)
r_{ia}	distance between electron i and nucleus a
r_b	distance between an electron and nucleus b
r_{12}	distance between electrons 1 and 2
R	internuclear separation
S	overlap integral
s	s-type atomic orbital
T_i	kinetic energy operator for electron i
x, y, z	abbreviated notation for the atomic functions p_x, p_y, and p_z; also Cartesian coordinates

α,β	spin functions
λ	variational parameter
ξ,ξ^*	molecular orbitals
$\pi_x,\pi_y,\pi_x^*,\pi_y^*$	π-type molecular orbitals
σ,σ^*	σ-type molecular orbitals
τ_i	volume element for electron i is $d\tau_i$
ϕ	interaction potential; sometimes used with subscripts a (attractive) and r (repulsive)
ϕ_d	London dispersion energy
ψ	wave function
ψ_1,ψ_2,ψ_3	special wave functions defined by equation (11)
ψ_I,ψ_{II}	special wave functions ψ_1 and $2^{-1/2}\left(\psi_2 + \psi_3\right)$, respectively

Special notations:

$^1\Sigma_g^+, {}^3\Sigma_u^+, {}^5\Sigma_g^+,$ $^7\Sigma_u^+, A\ {}^3\Sigma_u^+, X\ {}^1\Sigma_g^+$	molecular states
$^4S, {}^2D, {}^2P$	atomic states
$<\psi_i \vert H \vert \psi_j>$	Dirac integral defined by equation (C1)
$(xy \vert z)$	atomic state function defined by equation (B2)
1,2,3,4	sets of spatial coordinates for electrons 1, 2, 3, 4

Primes are used as indices to distinguish different functions.

ATOMIC AND MOLECULAR CORRELATIONS

With the z-axis defined as coincident with the line joining the two nuclei of a nitrogen molecule, the conventional molecular orbital (MO) notation of σ, σ^*, π_x, π_x^*, π_y, and π_y^* is chosen for the individual states accessible to the electrons of a p^3 configuration on each atom. The various two-electron bonding and antibonding possibilities are reviewed and summarized in appendix A, it being assumed that only the interactions between electrons in similarly oriented p-type atomic orbitals (AO) will contribute to the interatomic potentials. Overlap between the atomic orbitals of different atoms is the essential consideration.

As is explained also in appendix A, doubly occupied molecular orbitals such as $(\sigma)^2$ must not be regarded too literally at large distances because of the configuration interaction with $(\sigma^*)^2$; hence, the proper wave function for $(\sigma)^2$ is the valence bond (VB) expression $z_a(1)\, z_b(2) + z_b(1)\, z_a(2)$ constructed from p_z orbitals z_a and z_b centered, respectively, on the nuclei a and b. Likewise, with the understanding that all dissociations of present interest leave one electron in each of z_a and z_b, the triplet relation of equation (A4) is employed always in place of the singlet relation of equation (A5) for the notation $(\sigma)(\sigma^*)$. Similar statements apply to orbitals with other symmetries. Although the dissociation products of a given molecular state can be presented in a number of ways, corresponding to the various orientations of the individual atomic spins, only one set of atomic functions is ever required for the desired correlations. A complete listing of the pertinent atomic states is given in appendix B.

The following dissociations of molecular nitrogen are significant:

$$^1\Sigma_g^+:\quad (\sigma)^2\left(\pi_x\right)^2\left(\pi_y\right)^2 \longrightarrow \left(x_a y_a z_a\right) + \left(|x_b y_b z_b\right) \qquad (1)$$

$$^3\Sigma_u^+:\quad (\sigma)^2\left(\pi_x\right)^2\left(\pi_y\right)\left(\pi_y^*\right) \longrightarrow \left(x_a y_a z_a\right) + \left(y_b|z_b x_b\right) \qquad (2)$$

$$(\sigma)^2\left(\pi_x\right)\left(\pi_x^*\right)\left(\pi_y\right)^2 \longrightarrow \left(x_a y_a z_a\right) + \left(x_b|y_b z_b\right) \qquad (3)$$

$$(\sigma)(\sigma^*)\left(\pi_x\right)^2\left(\pi_y\right)^2 \longrightarrow \left(x_a y_a z_a\right) + \left(z_b|x_b y_b\right) \qquad (4)$$

$$^5\Sigma_g^+:\quad (\sigma)^2\left(\pi_x\right)\left(\pi_x^*\right)\left(\pi_y\right)\left(\pi_y^*\right) \longrightarrow \left(x_a y_a z_a\right) + \left(x_b y_b|z_b\right) \qquad (5)$$

$$(\sigma)(\sigma^*)\left(\pi_x\right)^2\left(\pi_y\right)\left(\pi_y^*\right) \longrightarrow \left(x_a y_a z_a\right) + \left(y_b z_b|x_b\right) \qquad (6)$$

$$(\sigma)(\sigma^*)\left(\pi_x\right)\left(\pi_x^*\right)\left(\pi_y\right)^2 \longrightarrow \left(x_a y_a z_a\right) + \left(z_b x_b|y_b\right) \qquad (7)$$

$$^{7}\Sigma_{u}^{+}:\quad (\sigma)(\sigma^{*})(\pi_{x})(\pi_{x}^{*})(\pi_{y})(\pi_{y}^{*}) \longrightarrow (x_{a}y_{a}z_{a}) + (x_{b}y_{b}z_{b}) \tag{8}$$

Each of the parentheses to the right of the arrows is symbolic of determinants defined as in equation (B2), the interconnecting positive signs between them referring schematically to $N_2 \rightarrow N + N$. The dissociations (2), (3), (6), and (7) are not deduced from pure molecular states but rather from mixtures of Σ and Δ symmetries; the correct combinations to establish definite Σ states occur automatically in the subsequent analysis.

It is noted that only the first atomic parentheses in each of the relations (2) to (7) represents an observed atomic state, namely, the $N\left[{}^{4}S\left(M_S = 3/2\right)\right]$ of equation (B6), whereas the second is only a part of equation (B4), (B5), (B7), or (B8). Accordingly, the following linear combinations are required:

$$\psi\left(X\ {}^{1}\Sigma_{g}^{+} \rightarrow {}^{4}S + {}^{4}S\right) = \psi\left[(\sigma)^{2}(\pi_{x})^{2}(\pi_{y})^{2}\right] \tag{9}$$

$$\begin{aligned}\psi\left(A\ {}^{3}\Sigma_{u}^{+} \rightarrow {}^{4}S + {}^{4}S\right) = {}& 3^{-1/2}\psi\left[(\sigma)^{2}(\pi_{x})^{2}(\pi_{y})(\pi_{y}^{*})\right] + 3^{-1/2}\psi\left[(\sigma)^{2}(\pi_{x})(\pi_{x}^{*})(\pi_{y})^{2}\right] \\ & + 3^{-1/2}\psi\left[(\sigma)(\sigma^{*})(\pi_{x})^{2}(\pi_{y})^{2}\right]\end{aligned} \tag{10}$$

$$\begin{aligned}\psi\left({}^{5}\Sigma_{g}^{+} \rightarrow {}^{4}S + {}^{4}S\right) = {}& 3^{-1/2}\psi\left[(\sigma)^{2}(\pi_{x})(\pi_{x}^{*})(\pi_{y})(\pi_{y}^{*})\right] + 3^{-1/2}\psi\left[(\sigma)(\sigma^{*})(\pi_{x})^{2}(\pi_{y})(\pi_{y}^{*})\right] \\ & + 3^{-1/2}\psi\left[(\sigma)(\sigma^{*})(\pi_{x})(\pi_{x}^{*})(\pi_{y})^{2}\right] \equiv 3^{-1/2}\left(\psi_{1} + \psi_{2} + \psi_{3}\right)\end{aligned} \tag{11}$$

and

$$\psi\left({}^{7}\Sigma_{u}^{+} \rightarrow {}^{4}S + {}^{4}S\right) = \psi\left[(\sigma)(\sigma^{*})(\pi_{x})(\pi_{x}^{*})(\pi_{y})(\pi_{y}^{*})\right] \tag{12}$$

where the notations ψ_1, ψ_2, and ψ_3 are defined in equation (11) for future reference and are considered to be orthonormal.

The coefficients on the right-hand sides of equations (10) and (11) are of equal magnitude because of the similar situations in equations (B7) and (B8); by way of contrast,

$$\begin{aligned}\psi\left({}^{5}\Sigma_{g}^{+} \rightarrow {}^{4}S + {}^{2}D\right) = {}& 2(6)^{-1/2}\psi\left[(\sigma)^{2}(\pi_{x})(\pi_{x}^{*})(\pi_{y})(\pi_{y}^{*})\right] - 6^{-1/2}\psi\left[(\sigma)(\sigma^{*})(\pi_{x})^{2}(\pi_{y})(\pi_{y}^{*})\right] \\ & - 6^{-1/2}\psi\left[(\sigma)(\sigma^{*})(\pi_{x})(\pi_{x}^{*})(\pi_{y})^{2}\right] \equiv 6^{-1/2}\left(2\psi_{1} - \psi_{2} - \psi_{3}\right)\end{aligned} \tag{13}$$

from equations (B4) and (5) to (7).

If the further definitions $\psi_I = \psi_1$ and $\psi_{II} = 2^{-1/2}\left(\psi_2 + \psi_3\right)$ are substituted into equations (11) and (13), there results

$$\psi\left({}^5\Sigma_g^+ \rightarrow {}^4S + {}^4S\right) = 3^{-1/2}\psi_I + (2/3)^{1/2}\psi_{II} \tag{14}$$

and

$$\psi\left({}^5\Sigma_g^+ \rightarrow {}^4S + {}^2D\right) = (2/3)^{1/2}\psi_I - 3^{-1/2}\psi_{II} \tag{15}$$

These expressions are identical with those of Mulliken (ref. 6) mentioned previously. A disadvantage of this notation with regard to intermolecular forces is discussed in the next section.

Finally, since $(\sigma)^2$ forms a stronger two-electron bond than either of $\left(\pi_x\right)^2$ or $\left(\pi_y\right)^2$ because of the greater overlap involved, an elementary consideration of the noncrossing rule for potential energy curves of the same symmetry yields the correlation diagrams

$$^5\Sigma_g^+:\quad \psi_I \longrightarrow 3^{-1/2}\psi_I + (2/3)^{1/2}\psi_{II}:\quad {}^4S + {}^4S \tag{16}$$

and

$$^5\Sigma_g^+:\quad \psi_{II} \longrightarrow (2/3)^{1/2}\psi_I - 3^{-1/2}\psi_{II}:\quad {}^4S + {}^2D \tag{17}$$

as the internuclear separation R increases from left to right. A similar procedure can be applied to the dissociations of $N_2\left(A\ {}^3\Sigma_u^+\right)$.

INTERACTION POTENTIALS

The combinations of electron configurations in equations (9) to (12), together with the two-electron bond and antibond energies (assumed to be additive) of appendix C, are sufficient to determine the long-range potentials of two colliding $N\left({}^4S\right)$ atoms. Equation (11) is preferred over equation (14) because the resonance implied by ψ_{II} between a single π_x bond and a single π_y bond is not so directly accessible to the simplest APP techniques as are the individual functions ψ_2 and ψ_3. In the final analysis, of course, the results must be equivalent.

One possible source for confusion remains. Since equations (11) and (13) are special examples of the more general variational function

$$\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3 \tag{18}$$

and since the variational process decrees that two of the coefficients C_1, C_2, and C_3 must vanish unless the energy integrals $<\psi_i|H|\psi_j>$ differ from zero when $i \neq j$, interactions between the individual configurations of ψ_1, ψ_2, and ψ_3 cannot be ignored in considerations of the total energy. At the large internuclear separations R of present interest, however, the sole function of such cross terms is the separation of the energy asymptotes corresponding to different dissociation products; accordingly, the interatomic forces are not affected. For comparatively small values of R, on the other hand, the cross term $<\psi_1|H|\psi_2 + \psi_3>$ has a negligible splitting effect because of the already large energy separation between the states ψ_I and ψ_{II}; this statement, in fact, is the explanation for ψ_I and ψ_{II} existing alone at the far left-hand sides of the correlation diagrams (16) and (17).

Hence, for the present application, the correct procedure is as follows: first, the APP interaction potentials are deduced independently for each substate in equations (9) to (12); secondly, these substate energies are given their proper statistical weights according to the squares of the coefficients of the corresponding wave functions; finally, the energies are added to yield the total interaction potentials. The results are:

$$\phi\left(X\ ^1\Sigma_g^+\right) = J_\sigma + 2J_\pi \tag{19}$$

$$\phi\left(A\ ^3\Sigma_u^+\right) = 3^{-1}\left(J_\sigma + J_\pi - J_\pi\right) + 3^{-1}\left(J_\sigma - J_\pi + J_\pi\right) + 3^{-1}\left(-J_\sigma + J_\pi + J_\pi\right) = 3^{-1}\left(J_\sigma + 2J_\pi\right) \tag{20}$$

$$\phi\left(^5\Sigma_g^+\right) = -3^{-1}\left(J_\sigma + 2J_\pi\right) \tag{21}$$

and

$$\phi\left(^7\Sigma_u^+\right) = -\left(J_\sigma + 2J_\pi\right) \tag{22}$$

where J_σ and J_π are exchange energies of the type J_2 in equation (C9). Improved estimates would include the London dispersion energy (Van der Waals attraction) in additive form (ref. 2).

For purposes of comparison, the energy

$$\phi\left(^5\Sigma_g^+ \rightarrow\ ^4S +\ ^2D\right) = 3^{-1}\left(J_\sigma - 4J_\pi\right) \tag{23}$$

is derived from equation (13). The interaction potential and the reference asymptote both differ from equation (21), even though the molecular state is $^5\Sigma_g^+$ in each case.

Although the physical origin of the exchange forces is made sufficiently clear by the Hellmann-Feynman electrostatic theorem (the enhancement of the negative charge distribution between nuclei in a bonding situation being related to the exchange forces, which, in turn, result from the particular mathematics of the VB procedure for satisfying Pauli's exclusion principle), detailed calculations involving equation (C9) are less useful than might be supposed. Computations based upon simple isolated hydrogen-like functions are too inaccurate. Nevertheless, as was shown first by Vanderslice, Mason, and Lippincott (ref. 7), much information can be obtained from expressions like equations (19) to (22) when they are employed judiciously with experimental data.

RELATIONS BETWEEN POTENTIALS

The most obvious characteristic of equations (19) to (22) is that the dependence upon J_σ and J_π is identical in the four states; accordingly,

$$\phi\left(A\ ^3\Sigma_u^+\right) = -\phi\left(^5\Sigma_g^+\right) = -3^{-1}\phi\left(^7\Sigma_u^+\right) = 3^{-1}\phi\left(X\ ^1\Sigma_g^+\right) \tag{24}$$

If the lowest potential curve is provided from ab initio quantum calculations (refs. 3 to 5), extrapolations of RKR results, or some other type of experimental data, the others are immediately available. Alternatively, delta function calculations (ref. 9) on the repulsive $^7\Sigma_u^+$ configuration could be used.

Vanderslice, Mason, and Lippincott (ref. 7), on the other hand, employed only the first substate in each of equations (10) and (11) to obtain

$$\phi\left(X\ ^1\Sigma_g^+\right) = J_\sigma + 2J_\pi \tag{25}$$

$$\phi\left(A\ ^3\Sigma_u^+\right) = J_\sigma \tag{26}$$

$$\phi\left(^5\Sigma_g^+\right) = J_\sigma - 2J_\pi \tag{27}$$

and

$$\phi\left(^7\Sigma_u^+\right) = -\left(J_\sigma + 2J_\pi\right) \tag{28}$$

They then deduced the final relations

$$\phi\left(^7\Sigma_u^+\right) = -\phi\left(X\ ^1\Sigma_g^+\right) \tag{29}$$

and

$$\phi\left(A\ ^3\Sigma_u^+\right) = 2^{-1}\left[\phi\left(^5\Sigma_g^+\right) - \phi\left(^7\Sigma_u^+\right)\right] = 2^{-1}\left[\phi\left(^5\Sigma_g^+\right) + \phi\left(X\ ^1\Sigma_g^+\right)\right] \tag{30}$$

each of which is included in equation (24). Aside from the greater complexity of equations (29) and (30), which presuppose the knowledge of two curves for a complete determination of the interactions between normal atoms, perhaps the most significant feature of the two sets of potentials is the additional symmetry provided by equations (20) and (21). Just as $X\ ^1\Sigma_g^+$ and $^7\Sigma_u^+$ are mirror images of each other across the dissociation asymptote, so are $A\ ^3\Sigma_u^+$ and $^5\Sigma_g^+$.

As previously explained by means of the correlation diagram (16) and a similar one for the $A\ ^3\Sigma_u^+$ state, a gradual transition must occur from equations (20) and (21) to equations (26) and (27) as R decreases; the present formulation, however, is expected to provide a better description over most of the range for which the valence bond theory is valid since it was designed for that purpose. A simple test of this prediction is furnished by numerical computations of the ratio of $\phi\left(X\ ^1\Sigma_g^+\right)$ to $\phi\left(A\ ^3\Sigma_u^+\right)$ according to three different methods: Vanderslice's formulation, the present formulation, and Gilmore's RKR extrapolations (ref. 8).

Because of the similarity of forms between J_σ and J_π and the fact that each is dependent dominantly upon the square of the corresponding overlap integral, J_π/J_σ can be replaced for present purposes with $\left(S_\pi/S_\sigma\right)^2$. Accordingly, the approach of reference 7 yields

$$r \equiv \frac{\phi\left(X\ ^1\Sigma_g^+\right)}{\phi\left(A\ ^3\Sigma_u^+\right)} = 1 + 2\left(\frac{J_\pi}{J_\sigma}\right) \approx 1 + 2\left(\frac{S_\pi}{S_\sigma}\right)^2 \approx 1 \tag{31}$$

for the desired ratio, whereas equations (19) and (20) give the constant value 3. Table I summarizes the various results and clearly supports the present technique over a wide range of the potential tails if Gilmore's curves are accurate. Vanderslice's formula does not agree with Gilmore's potentials where the VB theory is valid.

TABLE I.- RATIOS r OF $\phi\left(X\ ^1\Sigma_g^+\right)$ TO $\phi\left(A\ ^3\Sigma_u^+\right)$ AS FUNCTIONS OF THE INTERNUCLEAR SEPARATION R

R, angstroms	Ratios r from –		
	Equation (31)	Present paper	Reference 8
2.8	1.04	3.0	2.8
2.6	1.05	3.0	2.7
2.0	1.1	3.0	1.9

An interesting observation concerns the $^5\Sigma_g^+$ dissociation: Whereas equation (21) predicts a purely repulsive interaction, equation (27) states that the potential is attractive at large R because of the dominance of J_σ over J_π. A more realistic representation would retain the repulsion in the far regions, depict a maximum in the potential curve at a somewhat smaller separation, and culminate in a minimum between 1.5 and 1.6 angstroms (ref. 8) as the left-hand side of the correlation diagram (16) is approached. It appears doubtful that Gilmore's second minimum between 2.8 and 2.9 angstroms is realistic; in addition, he seems to underestimate the $^5\Sigma_g^+$ curve between 2.2 and 2.9 angstroms in violation of the requirement that the A $^3\Sigma_u^+$ potential should lie midway between those of X $^1\Sigma_g^+$ and $^5\Sigma_g^+$. Equations (29) and (30) are invariant in regard to the present and Vanderslice theories, and therefore are especially reliable.

Finally, if the London dispersion energy ϕ_d is added to each of equations (19) to (22) and then eliminated between combinations of the resulting expressions, the following relations are obtained between interaction potentials which include the effects of ϕ_d:

$$\phi\left(A\ {}^3\Sigma_u^+\right) = 2^{-1}\left[\phi\left(X\ {}^1\Sigma_g^+\right) + \phi\left({}^5\Sigma_g^+\right)\right] \tag{32}$$

and

$$\phi\left({}^5\Sigma_g^+\right) = 2^{-1}\left[\phi\left(A\ {}^3\Sigma_u^+\right) + \phi\left({}^7\Sigma_u^+\right)\right] \tag{33}$$

Equation (32) is common also to the analysis of reference 7 with or without ϕ_d, but equation (33) is unique to the current model.

CONCLUDING REMARKS

Valence-bond expressions have been derived for the outer regions of the four interaction potentials governing collisions between ground-state nitrogen atoms. Although the individual potential tails are probably not very accurate in an absolute sense, the relations obtained between the four energy states are expected to be reliable. Hence, the combination of the present results with a minimum amount of experimental data should prove adequate for most thermodynamic and kinetic-theory applications.

A principal advantage of the present method over the previous and similar work of Vanderslice, Mason, and Lippincott is the use of detailed correlations between the molecular states and the actual atomic products. The results of these correlations are distinguished by additional symmetries of the potential tails. Whereas Vanderslice, Mason, and Lippincott found only the most repulsive and most attractive potentials to be mirror images of each other, the present research predicts the same property also for the intermediate pair of curves. Finally, the intermediate potentials are expressed for the first time as simple fractions of the ground-state molecular energy and thus require less experimental data for the complete semiempirical specification of nitrogen collisions.

Langley Research Center,
National Aeronautics and Space Administration,
Hampton, Va., April 15, 1970.

APPENDIX A

THE HYDROGEN MOLECULE

A brief review of the essential features of two-electron molecular configurations (see ref. 10, pp. 340-358, for a more detailed description), especially in regard to the differences between molecular orbital (MO) and valence bond (VB) models, seems appropriate for this paper. The interaction energies of H_2 and several other simple molecules are derived in appendix C.

With $\xi = a + b$ and $\xi^* = a - b$ as the basic molecular orbits, where a and b are 1 s-atomic functions (AO) centered, respectively, on nuclei a and b, there are possible six different occupations by two electrons: both in ξ, both in ξ^*, one in ξ and the other in ξ^* with antiparallel spins, and three orientations of the parallel spin combination of one in ξ and one in ξ^*. Only four states of H_2 exist, however, one for the singlet $X\ {}^1\Sigma_g^+$ configuration and three for the triplet ${}^3\Sigma_u^+$, which dissociate into normal atoms; accordingly, two of the six MO occupations must yield excited products. A study of the configuration interaction between the first two occupations is essential for this distinction.

The expansion of the two-electron MO wave functions $\xi(1)\ \xi(2) = (\xi)^2$ and $\xi^*(1)\ \xi^*(2) = (\xi^*)^2$ gives

$$(\xi)^2 + \lambda(\xi^*)^2 = (1 - \lambda)\left[a(1)\ b(2) + b(1)\ a(2)\right] + (1 + \lambda)\left[a(1)\ a(2) + b(1)\ b(2)\right] \tag{A1}$$

where λ is a variational parameter and 1 and 2 refer to the electrons. At large internuclear separations (negligible overlap between a and b), the variational procedure selects $\lambda = -1$ and $\lambda = 1$ corresponding, respectively, to the H + H VB function $a(1)\ b(2) + b(1)\ a(2)$ and the $H^+ + H^-$ ionic state $a(1)\ a(2) + b(1)\ b(2)$. In addition, the application of the noncrossing rule reveals the correlation diagrams

$$H_2\left(X\ {}^1\Sigma_g^+\right):\quad (\xi)^2 \longrightarrow \text{valence bond:}\quad H + H \tag{A2}$$

and

$$H_2\left({}^1\Sigma_g^+\right):\quad (\xi^*)^2 \longrightarrow \text{ionic:}\quad H^+ + H^- \tag{A3}$$

for the transition from small to large distances.

The remaining occupations are, with their wave functions,

$$H_2\left({}^3\Sigma_u^+\right):\quad (\xi)(\xi^*) \longrightarrow \text{valence bond}\left[a(1)\ b(2) - b(1)\ a(2)\right]:\quad H + H \tag{A4}$$

and

$$H_2\left({}^1\Sigma_u^+\right): \quad (\xi)(\xi^*) \longrightarrow \text{ionic}\left[a(1)\,a(2) - b(1)\,b(2)\right]: \quad H^+ + H^- \qquad \text{(A5)}$$

Configuration interaction is not appropriate for either of the latter states; more specifically, the MO and VB descriptions are equivalent at all separations in the relation (A4).

APPENDIX B

WAVE FUNCTIONS FOR ATOMIC NITROGEN

The atomic eigenfunctions for the total angular momentum (quantum number L) of any complex species are obtained most directly by the technique of projection operators. With an arbitrary electron configuration in the linear vector space restricted to the total magnetic quantum number M_L equal to L, the subsequent operation (ref. 11) by

$$O_L = (2L + 1)! \sum_{t=0}^{L_{max}-L} \frac{(-1)^t L_-^t L_+^t}{t!(2L + t + 1)!} \tag{B1}$$

will select just that component of the Hilbert space representation of the initial wave function corresponding to the desired value of L. Other symbols are L_+ and L_-, the usual ladder operators of the electron system, and the maximum value L_{max} permitted for L. Operations by L_- are used for $M_L < L$.

As an example of the general procedure, the operator O_1 is applied to the three-electron function

$$(IO|O) = (3!)^{-1/2} \begin{vmatrix} I\alpha(1) & O\alpha(1) & O\beta(1) \\ I\alpha(2) & O\alpha(2) & O\beta(2) \\ I\alpha(3) & O\alpha(3) & O\beta(3) \end{vmatrix} \tag{B2}$$

where α and β are spin states and $I = x + iy$, $\bar{I} = x - iy$, and $O = z$, the x,y,z referring to p-type atomic functions of different orientations. With $L_{max} = 2$ because of Pauli's exclusion principle, the result of the projection operation is

$$\begin{aligned} \psi\left[{}^2P\left(M_L = 1\right)\right] &= 2^{-1/2}\left[(IO|O) + \left(\bar{I}I|I\right)\right] \\ &= 10^{-1/2}\left[2(xy|y) - (xz|z) - 2i(xy|x) - i(yz|z)\right] \end{aligned} \tag{B3}$$

The remaining functions of present interest for nitrogen are

$$\psi\left[{}^2D\left(M_L = 0,\ M_S = \frac{1}{2}\right)\right] = 6^{-1/2}\left[2(xy|z) - (zx|y) - (yz|x)\right] \tag{B4}$$

$$\psi\left[{}^2D\left(M_L = 0,\ M_S = -\frac{1}{2}\right)\right] = 6^{-1/2}\left[2(z|xy) - (y|zx) - (x|yz)\right] \tag{B5}$$

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$$\psi\left[{}^4S\left(M_S = \frac{3}{2}\right)\right] = (xyz) \tag{B6}$$

$$\psi\left[{}^4S\left(M_S = \frac{1}{2}\right)\right] = 3^{-1/2}\left[(xy|z) + (zx|y) + (yz|x)\right] \tag{B7}$$

$$\psi\left[{}^4S\left(M_S = -\frac{1}{2}\right)\right] = 3^{-1/2}\left[(x|yz) + (z|xy) + (y|zx)\right] \tag{B8}$$

and

$$\psi\left[{}^4S\left(M_S = -\frac{3}{2}\right)\right] = (|xyz) \tag{B9}$$

where M_S is the magnetic quantum number of the total spin. Step-down operators in spin space were employed for the derivation of equation (B5) from equation (B4) and equations (B7) to (B9) from equation (B6).

It is noted that the wave function for $N\left({}^2P\right)$ differs from those of $N\left({}^2D\right)$ and $N\left({}^4S\right)$ in two important ways: in the first place, the former is complex; secondly, it shows double occupations of the various p-atomic orbitals. Accordingly, the corresponding contributions to the interaction forces between two nitrogen atoms are not those of appendix C, but rather must be derived in similar fashion from the ionic functions in equations (A3) and (A5) of appendix A.

APPENDIX C

INTERACTION ENERGIES

Since the essence of most long-range molecular approximations is the neglect of overlap between unlike orbitals (differently oriented p-states, for example) on colliding atoms, so that each σ- or π-bond or antibond exists more or less independently of the others, only the interactions which arise from a given pair of similar atomic functions are considered in this appendix. All the pertinent behavior is deduced from a study of the one-, two-, three-, and four-electron occupations associated respectively with H_2^+, H_2, He_2^+, and He_2; in particular, theoretical relations between the different interaction energies are derived and compared with several techniques currently employed in the literature.

Integrals are expressed in the Dirac "bra-ket" notation defined by

$$<\psi\psi' \cdot \cdot \cdot|F|\psi''\psi''' \cdot \cdot \cdot> \equiv \int\left[\psi(1)\psi'(2) \cdot \cdot \cdot\right]^* F\left[\psi''(1)\psi'''(2) \cdot \cdot \cdot\right]d\tau_1\, d\tau_2 \cdot \cdot \cdot \tag{C1}$$

for the operator F and electrons 1, 2, · · · .

The Coulomb and exchange energies Q_i and J_i for an i-electron system are defined in terms of the attractive and repulsive interaction potentials ϕ_a and ϕ_r in the following manner:

$$Q_i = 2^{-1}\left(\phi_a + \phi_r\right) \tag{C2}$$

and

$$J_i = 2^{-1}\left(\phi_a - \phi_r\right) \tag{C3}$$

so that

$$\phi_{a,r} = Q_i \pm J_i \tag{C4}$$

A simple energy calculation involving the molecular orbitals a + b and a - b, where a and b are 1 s-atomic functions centered on the respective nuclei a and b, yields for the hydrogen molecule-ion H_2^+ the well-known expression

$$\phi_a = \frac{<a|H|a> + <a|H|b>}{1 + S} - E_o = \frac{<a|H|a>(1 + S) + <a|H|b> - S<a|H|a>}{1 + S} - E_o$$

$$= <a|H|a> - E_o + \frac{<a|H|b> - S<a|H|a>}{1 + S} = Q_1 + J_1 \tag{C5a}$$

and similarly,

$$\phi_r = \langle a|H|a\rangle - E_o - \frac{\langle a|H|b\rangle - S\langle a|H|a\rangle}{1 - S} = Q_1 - J_1 \tag{C5b}$$

Other symbols represent the full Hamiltonian operator H, the ground-state energy E_o of atomic hydrogen, and the overlap integral $S = \langle a|b\rangle$.

Equations (C2) and (C3) then give

$$Q_1 = \langle a|H|a\rangle - E_o - SJ_1 \approx e^2R^{-1} - e^2\langle a\left|r_b^{-1}\right|a\rangle \approx 0 \tag{C6}$$

and

$$J_1 = \left(1 - S^2\right)^{-1}\left(\langle a|H|b\rangle - S\langle a|H|a\rangle\right) \approx e^2S\langle a\left|r_b^{-1}\right|a\rangle - e^2\langle a\left|r_b^{-1}\right|b\rangle \tag{C7}$$

terms of order S^2 being neglected to the right of the approximate equalities in order to depict large internuclear separations R. The potential $-e^2r_b^{-1}$ refers to the interaction between the electron and nucleus b.

An exactly analogous manipulation for H_2, but this time with the valence-bond wave functions $a(1)\ b(2) \pm b(1)\ a(2)$ instead of molecular orbitals since the configuration interaction of appendix A destroys the latter concept at large R, yields

$$Q_2 = \langle ab|H|ab\rangle - 2E_o - S^2J_2 \approx e^2\langle ab\left|r_{12}^{-1}\right|ab\rangle - 2e^2\langle a\left|r_b^{-1}\right|a\rangle + e^2R^{-1} \approx 0 \tag{C8}$$

and

$$J_2 = \left(1 - S^4\right)^{-1}\left(\langle aa|H|bb\rangle - S^2\langle ab|H|ab\rangle\right) \approx e^2\langle aa\left|r_{12}^{-1}\right|bb\rangle - e^2S^2\langle ab\left|r_{12}^{-1}\right|ab\rangle + 2SJ_1 \tag{C9}$$

It is noted that whereas J_1 is of order S, J_2 approaches zero as S^2. This particular feature of long-range forces has been overlooked often in previous applications but is essential for subsequent comparisons. Such results, moreover, must not be confused with the statement (ref. 10, p. 362) that a two-electron bond is about twice as strong as the one-electron kind, for that conclusion is reached only by considering the near-equilibrium separations. At comparatively small values of R, the configuration interaction does not so disrupt the concept of a doubly occupied molecular orbital in the ground state of H_2; the triplet repulsive state, on the other hand, is still described by $a(1)\ b(2) - b(1)\ a(2)$ because

$$-\frac{1}{2}\begin{vmatrix} a(1) + b(1) & a(1) - b(1) \\ a(2) + b(2) & a(2) - b(2) \end{vmatrix} = \begin{vmatrix} a(1) & b(1) \\ a(2) & b(2) \end{vmatrix} \qquad \text{(C10)}$$

The electron wave function for He_2^+ may be written

$$\begin{vmatrix} [a(1) + b(1)]\alpha(1) & [a(1) - b(1)]\alpha(1) & [a(1) \pm b(1)]\beta(1) \\ [a(2) + b(2)]\alpha(2) & [a(2) - b(2)]\alpha(2) & [a(2) \pm b(2)]\beta(2) \\ [a(3) + b(3)]\alpha(3) & [a(3) - b(3)]\alpha(3) & [a(3) \pm b(3)]\beta(3) \end{vmatrix}$$

$$= -2\begin{vmatrix} a(1)\ \alpha(1) & b(1)\ \alpha(1) & [a(1) \pm b(1)]\beta(1) \\ a(2)\ \alpha(2) & b(2)\ \alpha(2) & [a(2) \pm b(2)]\beta(2) \\ a(3)\ \alpha(3) & b(3)\ \alpha(3) & [a(3) \pm b(3)]\beta(3) \end{vmatrix} \qquad \text{(C11)}$$

where α and β refer to the two spin orientations. Thus, as was shown first by Linnett (ref. 12), only one molecular orbital exists, the remaining two electrons occupying atomic functions (AO).

Since the AO electrons engage only in two-body exchange, which is of order S^2, it seems reasonable to assume for present purposes that their sole function is to screen perfectly (by one electron unit each) the nuclei from the MO electron. Accordingly, one should take the a and b of the latter to be hydrogen 1 s, drop all reference to the AO electrons except as they provide proton-like cores for the MO, and write $J_3 \approx J_1$. This procedure is supported also by the fact that the MO electron is likely to be found at distances farther from a nucleus than are those of atomic helium; consequently, the screening by the AO electrons is more effective in the molecule-ion.

A similar study of the electron wave function for He_2 reveals that no molecular orbital is formed, even at small internuclear separations. If the atomic functions a and b are defined so that

$$\left(T_1 + T_2 + e^2 r_{12}^{-1} - 2e^2 r_{1a}^{-1} - 2e^2 r_{2a}^{-1}\right) a(1)\ a(2) = E(\mathrm{He})\ a(1)\ a(2) \qquad \text{(C12)}$$

where T_i is the kinetic energy operator of electron i, there results

$$\phi_4 = Q_4 - J_4$$

$$Q_4 = \langle aabb|H|aabb\rangle - 2E(\mathrm{He}) = 4e^2\langle ab|r_{12}^{-1}|ab\rangle - 8e^2\langle a|r_b^{-1}|a\rangle + 4e^2R^{-1} \approx 0 \qquad \text{(C13)}$$

and

$$J_4 \approx 2\left(\langle aaab|H|abbb\rangle - S^2\langle aabb|H|aabb\rangle\right) = 4e^2S\langle aa\left|r_{12}^{-1}\right|ab\rangle + 2e^2\langle aa\left|r_{12}^{-1}\right|bb\rangle$$
$$- 6e^2S^2\langle ab\left|r_{12}^{-1}\right|ab\rangle + 4e^2S\left(S\langle a\left|2r_b^{-1}\right|a\rangle - \langle a\left|2r_b^{-1}\right|b\rangle\right) \tag{C14}$$

Contributions of order S^4 are neglected.

The substitution into equation (C14) of the approximate relation

$$2\langle aa\left|r_{12}^{-1}\right|ab\rangle \approx S\left(\langle aa\left|r_{12}^{-1}\right|aa\rangle + \langle ab\left|r_{12}^{-1}\right|ab\rangle\right) \tag{C15}$$

the foundation for which lies in the reasoning that $a(i)\ b(i)$ corresponds to electron i dividing its time equally between a and b, gives

$$J_4 \approx 2e^2\langle aa\left|r_{12}^{-1}\right|bb\rangle + 2e^2S^2\left(\langle aa\left|r_{12}^{-1}\right|aa\rangle - 2\langle ab\left|r_{12}^{-1}\right|ab\rangle\right) + 4e^2S\left(S\langle a\left|2r_b^{-1}\right|a\rangle - \langle a\left|2r_b^{-1}\right|b\rangle\right) \tag{C16}$$

As illustrated next, this form is a step closer to the application of screening arguments similar to those for He_2^+.

Because of the saturation of atomic orbitals in the present example, the neglect of terms of order S^4 in equation (C14) refers strictly to pairwise exchanges of electrons with parallel spins. If each such pair is assumed to simultaneously create an antibond and perfectly screen the nuclei as seen by the other pair, only the interactions between electrons with like spins will survive the setting of a and b in equation (C16) equal to hydrogen 1 s functions. In addition, $2e^2r_b^{-1}$ must be replaced by $e^2r_b^{-1}$ to yield

$$J_4 \approx 2e^2\langle aa\left|r_{12}^{-1}\right|bb\rangle - 2e^2S^2\langle ab\left|r_{12}^{-1}\right|ab\rangle + 4SJ_1 = 2J_2 \tag{C17}$$

A second way of reaching this same conclusion follows from the approximation of perfect pairing (APP) technique of Coulson (ref. 1) for the case of random spins. Since each electron of atom a pairs with each electron of atom b with one-fourth probability of antiparallel spins and three-fourths probability of parallel spins, there results

$$\phi_4 = 4\left(\frac{J_2}{4} - \frac{3J_2}{4}\right) = -2J_2 \tag{C18}$$

In summary, one can write

$$\phi_i = Q_i \pm J_i \qquad (i = 1, 2, \text{ or } 3)$$

$$\phi_4 = Q_4 - J_4$$

$$Q_i \approx 0$$

$$J_3 \approx J_1 = e^2\left(S\langle a\left|r_b^{-1}\right|a\rangle - \langle a\left|r_b^{-1}\right|b\rangle\right) \tag{C19}$$

and

$$J_4 \approx 2J_2 = 2\left(e^2\langle aa\left|r_{12}^{-1}\right|bb\rangle - e^2S^2\langle ab\left|r_{12}^{-1}\right|ab\rangle + 2SJ_1\right) \tag{C20}$$

at large internuclear separations. As mentioned previously, a significant feature is the fact that the first pair J_3 and J_1 of equation (C19) bears no simple relation to the second pair J_4 and J_2 of equation (C20); it is only when equilibrium results are extrapolated incorrectly to large distances (without accounting for the effects of configuration interaction upon MO theory) that $\phi_2 \approx 2\phi_1$ is obtained. Whereas the two-electron bond is stronger than the one-electron variety at short range, the roles are reversed further out.

The previous statements regarding the existence of only one molecular orbital in the case of He_2^+ and the failure of any to form for He_2 require additional explanation. An illustration of the pertinent facts is obtained most conveniently by means of the alternate forms of the two-electron determinant of equation (C10), according to which there are three methods of description as follows:

(a) Molecular orbital description: Apart from the net electron-electron interaction (assumed to be negligible for this discussion) in J_2, the assignment from equations (C4) and (C7) and the first form of equation (C6) of energy $J_1(1 - S)$ to the (a + b) electron and energy $-J_1(1 + S)$ to the (a - b) electron gives a total of $-2SJ_1 \approx -J_2$ for the two-electron antibond. Such additivity of independent one-electron energies is, of course, neither required nor implied by equation (C10), but is imposed in order to take full advantage of the molecular orbital notion.

(b) Valence bond description: This is the method of equations (C8) and (C9), which yields directly the antibond energy $-J_2$.

(c) Alternate molecular orbital description: The arbitrary assignment of energy $J_2/2$ to the (a + b) electron and energy $-3J_2/2$ to the (a - b) electron yields the correct antibond energy $-J_2$ without resort to the $-SJ_1$ portion of Q_1 used in description (a).

No allowance is made for the fact that $J_2/2$ and J_1 differ by at least the factor S. This technique is employed by Vanderslice, Mason, and Maisch in their work on nitric oxide (ref. 13) and oxygen (ref. 14).

Of the three procedures, description (b) is preferred because there is no tendency to ignore electron-electron interactions by pursuing too literally, as in (a), the concept of independent one-electron energies. Consequently, there is less danger in the assertion that molecular orbitals do not exist in such examples. Description (c), on the other hand, although equivalent to (a) in its results for $\phi_r(H_2)$ and $\phi(He_2)$ – visualize

$$\phi(He_2) = -J_4 = 2(J_2/2) + 2(-3J_2/2) = -2J_2$$

fails completely when the number of electrons is odd. More precisely, when one singly occupied MO is the essential feature, as in $\phi_a(H_2^+)$, $\phi_r(H_2^+)$, $\phi_a(He_2^+)$, and $\phi_r(He_2^+)$, description (c) gives the incorrect answers $J_2/2$, $-3J_2/2$, $-J_2/2$, and $-5J_2/2$, respectively. Each of these results disregards the factor S^{-1} and leads to serious difficulties, among which is the loss of the attractive character of $\phi_a(He_2^+)$. In addition, asymmetries are introduced between the bonds and antibonds of the same molecule.

Finally, should the electron-electron interactions of equation (C20) be comparable to $2SJ_1$, the literal interpretation of description (a) will be insufficient. A typical numerical calculation (see ref. 10, pp. 329, 342, and 343, for the appropriate integrals) at $R = 4$ atomic units shows that the neglected terms in (a) constitute about 40 percent of those retained; accordingly, J_i must be considered in at least the complexity suggested by equations (C19) and (C20). More elegant treatments, such as the generalization by Kolos and Wolniewicz (ref. 15) of the James and Coolidge wave function to large distances (keeping the dependence upon r_{12}), are required for absolute accuracy of the detailed characteristics (including the Van der Waals forces) of the potential tails.

These discussions, and especially the overlap distinctions between one- or three- and two- or four-electron configurations, are particularly significant for molecules in which two or more different types occur simultaneously. Previous calculations on the long-range interactions of nitrogen and oxygen (ref. 13) and two oxygen atoms (ref. 14), for example, must be reevaluated because of the relations employed between the two- and three-electron bonds and antibonds existing together in certain states.

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