N_2^+ POTENTIAL ENERGY CURVES

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ABSTRACT

A valence-bond method is used to determine a set of relations between the potential energies of those states of N_2^+ from which dissociation to ground state N and ground state N^+ takes place. The potential curves of the sextet and the quartet states are calculated at intermediate internuclear separation distances (2 Å - 3.5 Å) from these relations and the experimental curves of the doublet states.

If the interatomic potential energies for various values of the internuclear separation distance r are known, one can determine many collision processes when the translational energy is sufficiently low for the Born-Oppenheimer (adiabatic) approximation to be valid. For example, one can calculate elastic scattering cross sections, charge exchange cross sections, or transport cross sections from the potentials. Since nitrogen is the major constituent of air, the N^+-N potential energy (N_2^+ molecular eigenstate energy) is especially important for understanding atmospheric phenomena.[1,2] The object of the present work is to obtain potential curves for the collision of ground state N atoms and ions at fairly large values of r .

According to the Wigner-Witmer correlation rules, there are twelve different N_2^+ states for which the molecule dissociates into ground state atoms. Accurate potential curves of four of these, the doublet states, $^2\Sigma_g^+$, $^2\Sigma_u^+$, $^2\Pi_g$, and $^2\Pi_u$, have been computed from spectroscopic data for internuclear separation distances r near the equilibrium separation.[1,2,3,4] The potential curves for the remaining eight states with ground state dissociation products have been calculated[1,2] for large r from the doublet curves and potential relations which were derived by Knof, Mason, and Vanderslice[1] by valence bond theory. The latter results are not satisfactory, however, because they are based upon doublet molecular state functions that do not transform properly under inversion through the midpoint of the internuclear separation.

In the following analysis, N_2^+ potential energy relations are derived from wave functions that conform to the molecular symmetry.

As in the valence-bond method of Ref. 1, the N_2^+ state functions are constructed from linear combinations of Slater determinants of the valence orbitals of the ground states of the nitrogen atom $N(^4S^o)$ and ion $N^+(^3P$ From the twenty different determinants, one finds that general Σ state wave functions for $M_S = \frac{1}{2}$ which have the proper molecular symmetry properties can be written in the form:

$$\Phi_{u,g}^{S=1/2} = a\varphi_1 + b\varphi_2 + c\varphi_3 \tag{1a}$$

$$\Phi_{u,g}^{S=3/2} = d\varphi_4 + e\varphi_5 \tag{1b}$$

$$\Phi_{u,g}^{S=5/2} = \varphi_6 \tag{1c}$$

where

$$\varphi_1 = \frac{1}{\sqrt{18}}(3\Psi_1 - \Psi_2 - \Psi_3 - \Psi_4 + \Psi_5 + \Psi_6) \tag{2a}$$

$$\varphi_2 = \frac{1}{6}(\Psi_2 + \Psi_3 - 2\Psi_4 + 2\Psi_5 - 4\Psi_6) \tag{2b}$$

$$\varphi_3 = -\frac{1}{2}(\Psi_2 - \Psi_3) \tag{2c}$$

$$\varphi_4 = \frac{1}{\sqrt{90}}(6\Psi_1 + \Psi_2 + \Psi_3 + \Psi_4 - 4\Psi_5 - 4\Psi_6) \tag{2d}$$

$$\varphi_5 = \frac{1}{\sqrt{18}}(\Psi_2 + \Psi_3 - 2\Psi_4 - \Psi_5 + 2\Psi_6) \tag{2e}$$

$$\varphi_6 = \frac{1}{\sqrt{10}}(\Psi_1 + \Psi_2 + \Psi_3 + \Psi_4 + \Psi_5 + \Psi_6) \tag{2f}$$

and

$$\Psi_1 = |\pi_A^+ \bar{\pi}_B^+ \pi_A^- \bar{\pi}_B^- \sigma_A| \pm |\bar{\pi}_A^+ \pi_B^+ \bar{\pi}_A^- \pi_B^- \sigma_B| \tag{3a}$$

$$\Psi_2 = (|\pi_A^+ \pi_B^+ \bar{\pi}_A^- \bar{\pi}_B^- \sigma_A| + |\bar{\pi}_A^+ \bar{\pi}_B^+ \pi_A^- \pi_B^- \sigma_A|) \pm (|\pi_A^+ \pi_B^+ \bar{\pi}_A^- \bar{\pi}_B^- \sigma_B| \tag{3b}$$

$$+ |\bar{\pi}_A^+ \bar{\pi}_B^+ \pi_A^- \pi_B^- \sigma_B|)$$

$$\Psi_3 = \left(|\pi_A^+ \bar{\pi}_B^+ \bar{\pi}_A^- \pi_B^- \sigma_A| + |\bar{\pi}_A^+ \pi_B^+ \pi_A^- \bar{\pi}_B^- \sigma_A|\right) \pm \left(|\pi_A^+ \bar{\pi}_B^+ \bar{\pi}_A^- \pi_B^- \sigma_B| + |\bar{\pi}_A^+ \pi_B^+ \pi_A^- \bar{\pi}_B^- \sigma_B|\right) \tag{3c}$$

$$\Psi_4 = \left(|\pi_A^+ \pi_B^+ \pi_A^- \bar{\pi}_B^- \bar{\sigma}_A| + |\pi_A^+ \bar{\pi}_B^+ \pi_A^- \pi_B^- \bar{\sigma}_A|\right) \pm \left(|\pi_A^+ \pi_B^+ \bar{\pi}_A^- \pi_B^- \bar{\sigma}_B| + |\bar{\pi}_A^+ \pi_B^+ \pi_A^- \pi_B^- \bar{\sigma}_B|\right) \tag{3d}$$

$$\Psi_5 = \left(|\pi_A^+ \pi_B^+ \bar{\pi}_A^- \pi_B^- \bar{\sigma}_A| + |\bar{\pi}_A^+ \pi_B^+ \pi_A^- \pi_B^- \bar{\sigma}_A|\right) \pm \left(|\pi_A^+ \pi_B^+ \pi_A^- \bar{\pi}_B^- \bar{\sigma}_B| + |\pi_A^+ \bar{\pi}_B^+ \pi_A^- \pi_B^- \bar{\sigma}_B|\right) \tag{3e}$$

$$\Psi_6 = |\bar{\pi}_A^+ \pi_B^+ \bar{\pi}_A^- \pi_B^- \sigma_A| \pm |\pi_A^+ \bar{\pi}_B^+ \pi_A^- \bar{\pi}_B^- \sigma_B| \tag{3f}$$

The symbols on the right side of relation (3) have been defined in Ref. 1; e.g., $\bar{\sigma}$ ($\pi^{\pm}$) designates a 2p atomic orbital with the quantum numbers $m_s = -1/2$ and $m_\ell = 0$ ($m_s = 1/2$ and $m_\ell = \pm 1$), the subscripts A and B label the nuclei, and the vertical bars indicate that a Slater determinant is formed from the elements enclosed by them.

One sees from relation (1) that the wave functions of the sextet states are completely specified at this point, but those of the quartet and doublet states have one and two coefficients, respectively, to be determined. Since the potentials are to be calculated for fairly large r, the wave functions will be required to reduce to ground state atomic functions as r tends to infinity as in Mulliken's analysis[5] of the $^5\Sigma_g^+$ state of N_2. Following his work, one can rewrite the eigenfunctions (2) as

$$\varphi_1 = (1 \pm P_{AB})A_S\left[\frac{1}{\sqrt{2}}\Psi_A^{\frac{3}{2}}(^4S)\Psi_B^{-1}(^3P) - \frac{1}{\sqrt{3}}\Psi_A^{\frac{1}{2}}(^4S)\Psi_B^{0}(^3P) + \frac{1}{\sqrt{6}}\Psi_A^{-\frac{1}{2}}(^4S)\Psi_B^{1}(^3P)\right] \tag{4a}$$

$$\varphi_2 = (1 \pm P_{AB})A_S\left[\frac{1}{\sqrt{3}}\Psi_A^{\frac{1}{2}}({}^2D)\Psi_B^{0}({}^3P) - \sqrt{\frac{2}{3}}\,\Psi_A^{-\frac{1}{2}}({}^2D)\Psi_B^{1}({}^3P)\right] \tag{4b}$$

$$\varphi_3 = (1 \pm P_{AB})A_S\left[\frac{1}{\sqrt{3}}\Psi_A^{\frac{1}{2}}({}^2P)\Psi_B^{0}({}^1D) + \sqrt{\frac{2}{3}}\,\Psi_A^{\frac{1}{2}}({}^2P)\Psi_B^{0}({}^1S)\right] \tag{4c}$$

$$\varphi_4 = (1 \pm P_{AB})A_S\left[\sqrt{\frac{2}{5}}\,\Psi_A^{\frac{3}{2}}({}^4S)\Psi_B^{-1}({}^3P) + \frac{1}{\sqrt{15}}\Psi_A^{\frac{1}{2}}({}^4S)\Psi_B^{0}({}^3P) - \sqrt{\frac{8}{15}}\,\Psi_A^{-\frac{1}{2}}({}^4S)\Psi_B^{1}({}^3P)\right] \tag{4d}$$

$$\varphi_5 = (1 \pm P_{AB})A_S\left[\sqrt{\frac{2}{3}}\Psi_A^{\frac{1}{2}}({}^2D)\Psi_B^{0}({}^3P) + \sqrt{\frac{1}{3}}\Psi_A^{-\frac{1}{2}}({}^2D)\Psi_B^{1}({}^3P)\right] \tag{4e}$$

$$\varphi_6 = (1 \pm P_{AB})A_S\left[\frac{1}{\sqrt{10}}\Psi_A^{\frac{3}{2}}({}^4S)\Psi_B^{-1}({}^3P) + \sqrt{\frac{3}{5}}\Psi_A^{\frac{1}{2}}({}^4S)\Psi_B^{0}({}^3P) + \sqrt{\frac{3}{10}}\,\Psi_A^{-\frac{1}{2}}({}^4S)\Psi_B^{1}({}^3P)\right] \tag{4f}$$

where $\Psi_A^{m_s}$ $(\Psi_B^{m_s})$ are spin and orbital angular momentum eigenfunctions of an N atom (N^+ ion) with $m_\ell = 0$ and nuclear center A(B).[6,7] These atomic wavefunctions are expressed as linear combinations of second or third order determinants by Slater on page 308 of Ref. 7. The operator P_{AB} changes the subscript A into B or vice versa and A_S is a supplementary antisymmetrization operator. From the relations (4), it can be seen that the ground state dissociation requirement is satisfied by $\Phi_{u,g}^{5/2}$; the wavefunctions $\Phi_{u,g}^{3/2}$ and $\Phi_{u,g}^{1/2}$ will be made to satisfy this requirement also by the condition

$$b = c = e = 0 \tag{5}$$

The sextet states of Ref. 1 for $M_S = 5/2$ are equivalent to those of relation (1c). The quartet states of Ref. 1 correspond to the wavefunction (1b) when $d/e = -1/\sqrt{5}$; i.e., they contain a contribution from the excited state ^2D of the N atom.

Similarly, one can construct wavefunctions for the Π states that have the correct symmetry properties and that dissociate into ground state atomic wave functions as done for the Σ states above. The result can be expressed by the wavefunctions that one obtains by combining the relations (1), (2), and (5) when the Ψ_i take the form:

$$\Psi_1 = |\sigma_A \bar{\sigma}_B \pi_A^+ \bar{\pi}_B^+ \pi_A^-| \pm |\bar{\sigma}_A \sigma_B \bar{\pi}_A^+ \pi_B^+ \pi_B^-| \tag{6a}$$

$$\Psi_2 = (|\sigma_A \sigma_B \bar{\pi}_A^+ \bar{\pi}_B^+ \pi_A^-| + |\bar{\sigma}_A \bar{\sigma}_B \pi_A^+ \pi_B^+ \pi_A^-|) \pm (|\sigma_A \sigma_B \bar{\pi}_A^+ \bar{\pi}_B^+ \pi_B^-| \quad |\bar{\sigma}_A \bar{\sigma}_B \pi_A^+ \pi_B^+ \pi_B^-|) \tag{6b}$$

$$\Psi_3 = (|\sigma_A \bar{\sigma}_B \bar{\pi}_A^+ \pi_B^+ \pi_A^-| + |\bar{\sigma}_A \sigma_B \pi_A^+ \bar{\pi}_B^+ \pi_A^-|) \pm (|\sigma_A \bar{\sigma}_B \bar{\pi}_A^+ \pi_B^+ \pi_B^-| + |\bar{\sigma}_A \sigma_B \pi_A^+ \bar{\pi}_B^+ \pi_B^-|) \tag{6c}$$

$$\Psi_4 = (|\sigma_A \sigma_B \pi_A^+ \bar{\pi}_B^+ \bar{\pi}_A^-| + |\sigma_A \bar{\sigma}_B \pi_A^+ \pi_B^+ \bar{\pi}_A^-|) \pm (|\sigma_A \sigma_B \bar{\pi}_A^+ \pi_B^+ \bar{\pi}_B^-| + |\bar{\sigma}_A \sigma_B \pi_A^+ \pi_B^+ \bar{\pi}_B^-|) \tag{6d}$$

$$\Psi_5 = (|\sigma_A \sigma_B \bar{\pi}_A^+ \pi_B^+ \bar{\pi}_A^-| + |\bar{\sigma}_A \sigma_B \pi_A^+ \pi_B^+ \bar{\pi}_A^-|) \pm (|\sigma_A \sigma_B \pi_A^+ \bar{\pi}_B^+ \bar{\pi}_B^-| + |\sigma_A \bar{\sigma}_B \pi_A^+ \pi_B^+ \bar{\pi}_B^-|) \tag{6e}$$

$$\Psi_6 = |\bar{\sigma}_A \sigma_B \bar{\pi}_A^+ \pi_B^+ \pi_A^-| \pm |\sigma_A \bar{\sigma}_B \pi_A^+ \bar{\pi}_B^+ \pi_B^-| \tag{6f}$$

As in Ref. 1, the Hamiltonian for the system under consideration is taken to be

$$H = - \sum_{i=1}^{5} \left(\frac{1}{2} \nabla_i^2 + \frac{Z_A}{r_{Ai}} + \frac{Z_B}{r_{Bi}} \right) + \sum_{i<j} \frac{1}{r_{ij}} + \frac{Z_A Z_B}{r} \quad . \tag{7}$$

with $Z_A = Z_B = 3$. Then using the wave functions given above, one can calculate the potential energies and express the result in the form:

$$V_{u,g}^{S}(r) = \frac{W_0 + \frac{1}{3}W_2 + \frac{1}{3}W_4 \pm \frac{1}{3}(W_1 + W_3 + 3W_5)}{1 + \frac{1}{3}S_2 + \frac{1}{3}S_4 \pm \frac{1}{3}S_1(1 + S_2 + 3S_4)}, \quad S = 1/2 \tag{8a}$$

$$= \frac{W_0 - \frac{1}{6}W_2 - \frac{2}{3}W_4 \mp \frac{2}{3}(W_1 + \frac{1}{4}W_3 - \frac{3}{2}W_5)}{1 - \frac{1}{6}S_2 - \frac{2}{3}S_4 \mp \frac{2}{3}S_1(1 + \frac{1}{4}S_2 - \frac{3}{2}S_4)}, \quad S = 3/2 \tag{8b}$$

$$= \frac{W_0 - W_2 + W_4 \pm (W_1 - W_3 + W_5)}{1 - S_2 + S_4 \pm S_1(1 - S_2 + S_4)}, \quad S = 5/2 \tag{8c}$$

where the quantities W_i and S_i contain those terms in which i electrons are exchanged among the nuclei.

For Σ states

$$S_1 = S_\sigma, \; S_2 = 2S_\pi^2, \; S_4 = S_\pi^4$$

$$W_0 = \langle \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_A | H | \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_A \rangle - E_\infty - 2(g_1 + g_2) \tag{9}$$

$$W_1 = \langle \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_A | H | \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_B \rangle - E_\infty S_\sigma - 4\ell_3 - 2g_2 S_\sigma$$
$$+ 2q_1 S_\pi$$

$$W_2 = 2\langle \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_A | H | \pi_B^+ \pi_A^+ \pi_A^- \pi_B^- \sigma_A \rangle - 2E_\infty S_\pi^2 + 2(k_1 + k_2)$$
$$- 4(2\ell_1 + \ell_2)S_\pi - 2(g_1 - q_2)S_\pi^2$$

$$W_3 = 2\langle \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_A | H | \pi_B^+ \pi_A^+ \pi_A^- \pi_B^- \sigma_B \rangle - 2E_\infty S_\pi^2 S_\sigma + 2k_1 S_\sigma$$
$$- 2k_4 S_\pi - 8\ell_1 S_\pi S_\sigma - 4\ell_3 S_\pi^2 + 2q_1 S_\pi^3 + 2q_2 S_\pi^2 S_\sigma$$

$$W_4 = \langle \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_A | H | \pi_B^+ \pi_A^+ \pi_B^- \pi_A^- \sigma_A \rangle - E_\infty S_\pi^4 + 2(k_2 - k_3)S_\pi^2$$
$$- 4\ell_2 S_\pi^3$$

$$W_5 = \langle \pi_A^+ \pi_B^+ \pi_A^- \pi_B^- \sigma_A | H | \pi_B^+ \pi_A^+ \pi_B^- \pi_A^- \sigma_B \rangle - E_\infty S_\pi^4 S_\sigma + 2k_3 S_\pi^2 S_\sigma$$
$$+ 2k_4 S_\pi^3$$

and for Π states

$$S_1 = S_\pi\,,\ S_2 = S_\pi^2 + S_\sigma^2,\ S_4 = S_\pi^2 S_\sigma^2$$

$$W_0 = \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- \rangle - E_\infty - 3g_1 - g_2$$

$$W_1 = \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_B^- \rangle - E_\infty S_\pi - 2(\ell_1 + \ell_2)$$

$$- (2g_1 - q_2)S_\pi + q_1 S_\sigma$$

$$W_2 = \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_B\sigma_A\pi_A^+\pi_B^+\pi_A^- \rangle + \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_A\sigma_B\pi_B^+\pi_A^+\pi_A^- \rangle$$

$$-E_\infty(S_\pi^2 + S_\sigma^2) + k_1 + 3k_2 - 2(\ell_1 + 2\ell_2)S_\pi - 6\ell_3 S_\sigma - g_1 S_\pi{}^2 - g_2 S_\sigma{}^2 + 2q_1 S_\pi S_\sigma$$

$$W_3 = \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_B\sigma_A\pi_A^+\pi_B^+\pi_B^- \rangle + \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_A\sigma_B\pi_B^+\pi_A^+\pi_B^- \rangle$$

$$- E_\infty(S_\pi{}^2 + S_\sigma{}^2)S_\pi + (2k_2 - k_3)S_\pi - k_4 S_\sigma - 2\ell_1 S_\sigma{}^2 - 6\ell_2 S_\pi{}^2 - 4\ell_3 S_\pi S_\sigma$$

$$+ 3q_1 S_\pi{}^2 S_\sigma + q_2 S_\pi S_\sigma{}^2$$

$$W_4 = \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_B\sigma_A\pi_B^+\pi_A^+\pi_A^- \rangle - E_\infty S_\pi{}^2 S_\sigma{}^2 + k_1 S_\sigma{}^2 + k_2 S_\pi{}^2 - 2k_4 S_\pi S_\sigma$$

$$- 2\ell_1 S_\pi S_\sigma{}^2 - 2\ell_3 S_\pi{}^2 S_\sigma$$

$$W_5 = \langle \sigma_A\sigma_B\pi_A^+\pi_B^+\pi_A^- | H | \sigma_B\sigma_A\pi_B^+\pi_A^+\pi_B^- \rangle - E_\infty S_\pi{}^3 S_\sigma{}^2 + k_3 S_\pi S_\sigma{}^2 + 3k_4 S_\pi{}^2 S_\sigma$$

where the overlap integrals are

$$S_\sigma = \langle \sigma_A | \sigma_B \rangle, \quad S_\pi = \langle \pi_A^+ | \pi_B^+ \rangle$$

the two electron integrals are

$$g_1 = \langle \pi_A^+\sigma_A | 1/r_{12} | \sigma_A\pi_A^+ \rangle \qquad q_1 = \langle \pi_A^+\sigma_B | 1/r_{12} | \sigma_A\pi_B^+ \rangle$$

$$g_2 = \langle \pi_A^+\pi_A^- | 1/r_{12} | \pi_A^-\pi_A^+ \rangle \qquad q_2 = \langle \pi_A^+\pi_B^- | 1/r_{12} | \pi_A^-\pi_B^+ \rangle$$

$$k_1 = \langle \pi_A^+ \pi_B^- | 1/r_{12} | \pi_B^- \pi_A^+ \rangle \qquad \ell_1 = \langle \pi_A^+ \pi_A^- | 1/r_{12} | \pi_A^- \pi_B^+ \rangle$$

$$k_2 = \langle \pi_A^+ \sigma_B | 1/r_{12} | \sigma_B \pi_A^+ \rangle \qquad \ell_2 = \langle \pi_A^+ \sigma_A | 1/r_{12} | \sigma_A \pi_B^+ \rangle$$

$$k_3 = \langle \pi_A^+ \pi_A^- | 1/r_{12} | \pi_B^- \pi_B^+ \rangle \qquad \ell_3 = \langle \pi_A^+ \sigma_A | 1/r_{12} | \sigma_B \pi_A^+ \rangle$$

$$k_4 = \langle \pi_A^+ \sigma_A | 1/r_{12} | \sigma_B \pi_B^+ \rangle$$

and E_∞ is the sum of the energies of the free atom and ion.

For large values of r the contribution to the interaction energy from the coulomb integrals W_0 and from the terms which involve more than two electron exchange integrals is small compared to that from the one and two electron exchange integrals.[7,8] The value of S_1 is also small for large r; e.g., from the analytic Hartree Fock atomic wave functions of Clementi,[9] one finds that S_1 is small compared to unity for $r \gtrsim 2$ Å. Hence, for large r, the potential energies (8) can be approximated by

$$V^S_{u,g}(r) \rightarrow \frac{1}{3}W_2 \pm \frac{1}{3}W_1 , \quad S = \frac{1}{2} \tag{10a}$$

$$\rightarrow \frac{1}{6}W_2 \mp \frac{2}{3}W_1 , \quad S = \frac{3}{2} \tag{10b}$$

$$\rightarrow -W_2 \pm W_1 , \quad S = \frac{5}{2} \tag{10c}$$

The values of W_1 and W_2 were first calculated from relation (10a) and the spectroscopic doublet state curves calculated by Gilmore,[2] and then the potential curves of the sextet and doublet states were calculated from the relations (10b) and (10c). The results are shown in Fig. 1. The order of the quartet states is opposite that of Ref. 1; i e., the ${}^4\Sigma_g^+$ and ${}^4\Pi_u$ lie above the ${}^4\Sigma_u^+$ and ${}^4\Pi_g$ states. This is consistent with Gilmore's prediction that these latter two are bound states. In addition, if the quartet potential curves are extended to smaller r using relation (10) and the spectroscopic curves, one finds that the minimum of the $^4\Sigma_u^+$ potential would occur at $r \sim 1.3$ Å and that of the $^4\Pi_g$ state at $r < 1.3$ Å which is in good agreement with Gilmore's estimated values.

In regard to gas dynamic calculations, one can see that the sextet states will dominate the large angle elastic scattering because of their high spin multiplicity and their large repulsive potentials (see Fig. 1). Also, one can note that N^+-N charge exchange cross sections may be calculated directly from the doublet spectroscopic curves and the relation (10), if the Σ state extrapolation procedure of Ref. 1 is followed.

Reference

[1] Hans Knof, E. A. Mason, and J. T. Vanderslice, J. Chem. Phys. 40 3548 (1964).

[2] Forest R. Gilmore, J. Quant. Spectrosc. Radiat. Transfer 5 369 (1965).

[3] T. Namioka, K. Yoshino, and Y. Tanaka, J. Chem. Phys. 39 2629 (1963).

[4] Ran B. Singh and D. K. Rai, J. Mol. Spectrosc. 19 424 (1966).

[5] Robert S. Mulliken, J. Chem. Phys. 37 809 (1962).

[6] John C. Slater, Quantum Theory of Atomic Structure, Vols. I and II (McGraw-Hill Book Co. Inc., New York, 1960).

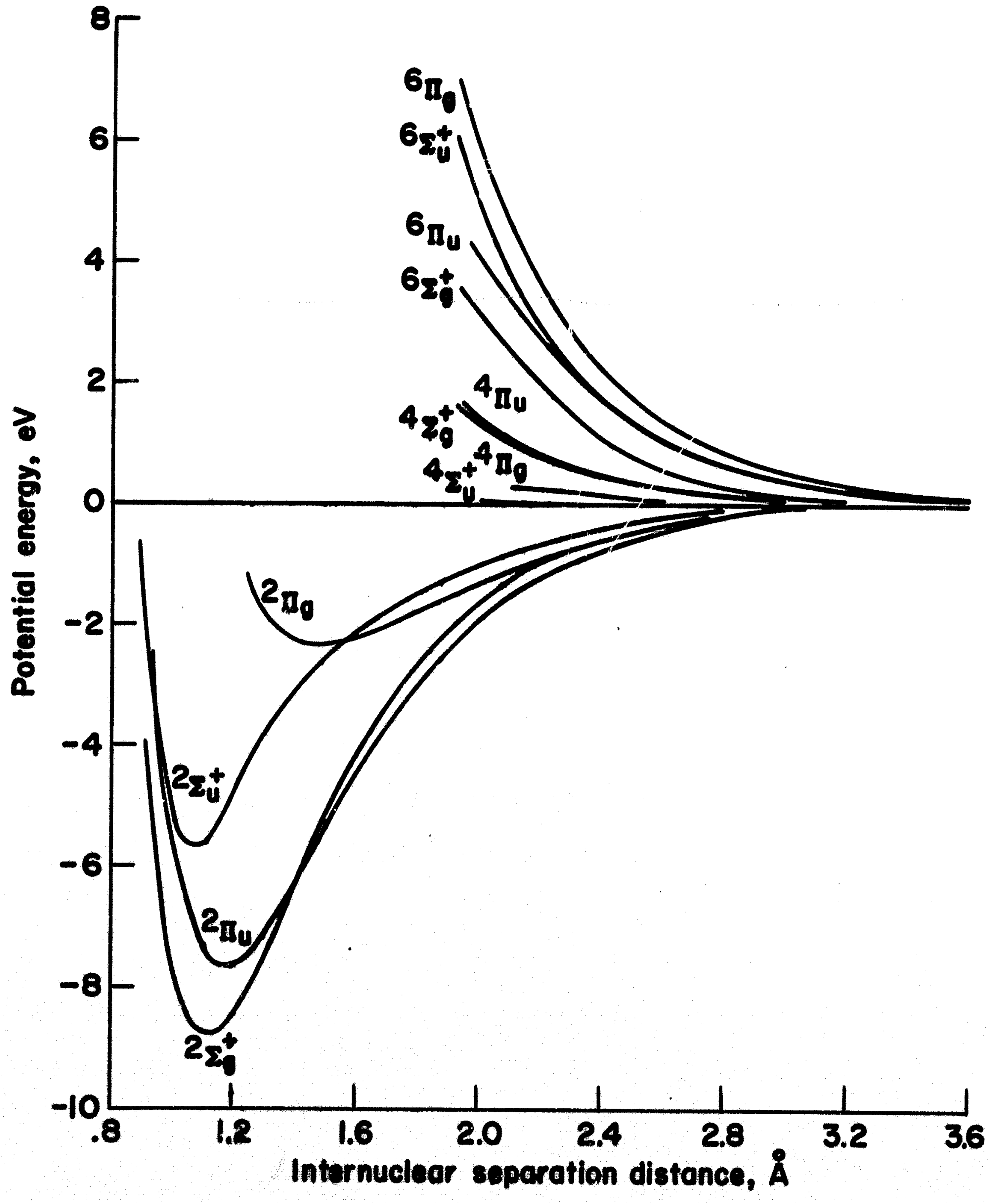
[7] John C. Slater, Quantum Theory of Molecules and Solids, Vol. I (McGraw-Hill Book Co. Inc., New York, 1963).

[8] Henry Eyring, John Walter, and George E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., 1964).

[9] Enrico Clementi, "Tables of Atomic Functions", Supplement to IBM J. Res. Dev. 9 2 (1965).

FIGURE TITLE

Figure 1. Potential energy curves for $N_2^+ \rightarrow N(^4S^o) + N^+(^3P)$.



$^6\Pi_g$
$^6\Sigma_u^+$
$^6\Pi_u$
$^6\Sigma_g^+$
$^4\Pi_u$
$^4\Sigma_g^+$
$^4\Pi_g$
$^4\Sigma_u^+$
$^2\Pi_g$
$^2\Sigma_u^+$
$^2\Pi_u$
$^2\Sigma_g^+$
8
6
4
2
0
-2
-4
-6
-8
-10
Potential energy, eV
.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
Internuclear separation distance, Å

Fig. 1