

N⁺-N long-range interaction energies and resonance charge exchange

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The aerothermodynamic studies of proposed space missions require atmospheric charge-transfer data. N₂⁺ eigenstate energies are calculated with use of the complete-active-space self-consistent-field method with an extended Gaussian basis set. The N⁺-N charge-exchange cross section, determined from these energies, agrees with merged-beam measurements. This contradicts the previous theoretical conclusion. A simple physical description of the long-range interaction is presented and should expedite future charge-transfer studies.

Resonance charge exchange is an important mechanism in determining the properties of nonequilibrium partially ionized gases that are expected to occur in the environment of high altitude flight paths of aero-assist orbital transfer vehicles (AOTV's) proposed to transport men and materials between the space station and distant points, including geosynchronous orbit and the moon. Since nitrogen is the major constituent of air, the N⁺-N charge exchange is especially important for aerothermodynamic studies of these missions.

The N₂⁺ eigenstate energies for large internuclear separation distances are needed to determine the N⁺-N charge-exchange cross section. Stallcop¹ has developed asymptotic relations for these energies from a Heitler-London-valence-bond approach. These relations were combined with potential-energy curves for the doublet states, obtained from an extrapolation of spectroscopic data, to estimate² the charge-exchange cross section. Later, Capitelli *et al.*³ applied the valence-bond eigenstates of Stallcop¹ to compute energies with a minimal Slater-type orbital basis set. They compared their calculated cross section with that measured by Belyaev, Brezhnev, and Erastov⁴ using a merged-beam experiment, concluded that the measured values are too large, and suggested that the experiment be redone.

In a systematic investigation, we have calculated the complete set of N₂⁺ potential-energy curves for which the molecule dissociates into N(⁴S^o) and N(³P). With respect to charge exchange, we conclude that the valence-bond wave functions would provide a fairly accurate low-

resolution charge-exchange cross section σ_{ex} , but that it requires careful attention to the physics of the long-range interaction; particularly, when the calculation is performed with a small basis set such as in Ref. 3.

At high collision energies only the splitting energy, the energy difference between the interaction energies of the symmetric and antisymmetric states, $E_g^{\Lambda,S}(R)$ and $E_u^{\Lambda,S}(R)$, respectively, is required to determine the low-resolution charge-exchange cross section. According to our valence-bond formulation,¹ this splitting takes a simple form for large R

$$\Delta E_{\Lambda}^{2s+1}(R) = E_u^{\Lambda,S}(R) - E_g^{\Lambda,S}(R) \rightarrow -\frac{1}{3}(-1)^{2S+1}(2S+1)W_{\Lambda}(R), \quad (1)$$

where $W_{\Lambda}(R)$ contains the single electron exchange terms. In Table I, we compare this prediction with the results of a corresponding structure calculation, complete-active-space self-consistent-field (CASSCF) computation with only $2p$ valence electrons active. Note that the ratio of the splittings converges to the valence-bond value with increasing R . This suggests that the interaction at large R is essentially hydrogenic; i.e., like H⁺-H where the Heitler-London approximation⁶ yields

$$\Delta E(R) \rightarrow \frac{8\pi}{3} R e^{-\alpha R}, \quad \text{as } \alpha \rightarrow 1, \quad R \rightarrow \infty. \quad (2)$$

Using this hydrogenic model as a rough guide to convergence, we note that smaller basis sets, even though they yield good agreement (~ 0.1 eV) with spectroscopic curves

TABLE I. Ratio of N₂⁺ u - g splittings from a CASSCF calculation with a $[4s3p1d]$ Gaussian basis set. This basis set consists of $(9s5p)$ contracted to $[4s3p]$ (Ref. 5) and a d -function with shielding constant 0.9. The valence-bond (VB) ratio is determined from relation (1).

$R(a_0)$		4	5	6	7	8	10	VB
$-\Delta E^4/\Delta E^2$	Σ	2.05	2.10	2.04	2.01	2.00	2.00	2
	Π	1.78	1.95	2.00	2.00	2.00	2.00	2
$-\Delta E^6/\Delta E^4$	Σ	2.40	1.77	1.56	1.52	1.50	1.50	1.5
	Π	1.38	1.46	1.50	1.50	1.50	1.50	1.5

at small R , can be inadequate at large R . In Fig. 1, we show the results of a CASSCF calculation with both the $2s$ and $2p$ electrons relaxed and using an extensive basis set ($6s4p3d1f$); i.e., ($11s7p$) contracted⁷ to $[5s3p]$, augmented by ($1d,1f$), plus additional ($1s1p2d$) field induced polarization functions. More information about this basis set and the computer codes of the present calculation is contained in the paper by Langhoff, Bauschlicher, and Chong⁸ which also presents an application to the determination of N_2 polarizabilities. We expect the Σ state interactions, which are the dominant contributors to charge exchange, to resemble hydrogen⁹ and have used this to fit their curves to the computed points. Note the simple uniform behavior of the splitting energy at large R : (i) the ratio of the splitting for different spin states is about that predicted by the valence-bond relation (1) above, (ii) the ${}^6\Sigma$ splitting is very close to hydrogen [i.e., see relation (2) noting that $8\pi/3 \approx 2.66$], and (iii) the splitting of the Σ states is roughly a factor R larger than those for the Π states.

The exponential behavior of the splitting further suggests that the induced polarizability satisfies $\alpha_g \approx \alpha_u$ for each of the angular momentum pairs. If we apply our asymptotic valence-bond relations¹ to subtract the electron exchange [$\approx \Delta E(R)/2$] from the calculated interaction, we find that the difference has a $1/R^4$ dependence and indeed, as might

be expected, that $\alpha_g = \alpha_u$ to the accuracy of the curve fit shown in Fig. 1.

For a first approximation of the charge-transfer cross section, we replace the sine² dependence of the charge-exchange probability as small impact parameters [e.g., see Eq. (10) of Ref. 10] by the average value $\frac{1}{2}$. This low-resolution cross section can then be readily obtained from the curve fits of Fig. 1 by the relations¹⁰

$$\sigma_{ex}(v) = \frac{1}{2} \pi b_c^2, \quad (3)$$

where the cut-off impact parameter b_c satisfies

$$b_c^{2n+1} e^{-2\alpha b_c} = \frac{\pi}{8} \frac{h^2 v^2}{A^2} \alpha, \quad (4)$$

when the energy difference has an exponential dependence, i.e.,

$$\Delta E(R) = AR^n e^{-\alpha R}, \quad n=0,1. \quad (5)$$

Combining the parameters shown in Fig. 1 with the above relations, we calculate the cross section for each pair of angular momentum states and plot the results in Fig. 2. Note that the behavior of the cross sections reflects the uniform behavior of the energy splittings discussed above.

The measured cross section is the statistical average of

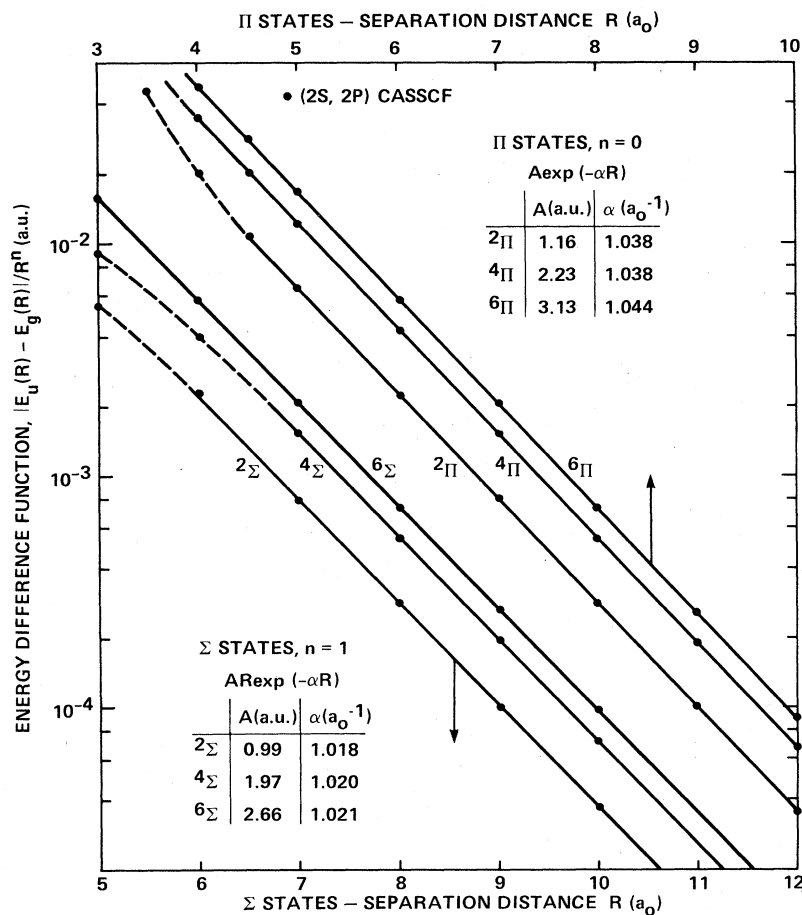


FIG. 1. N_2^+ energy differences for large R . The calculated values are plotted as data points and the straight lines are the curve fits from the tabulated parameters. Note that the abscissa for the Π state curves has been offset with respect to that for the Σ states.

N⁺ - N CHARGE TRANSFER

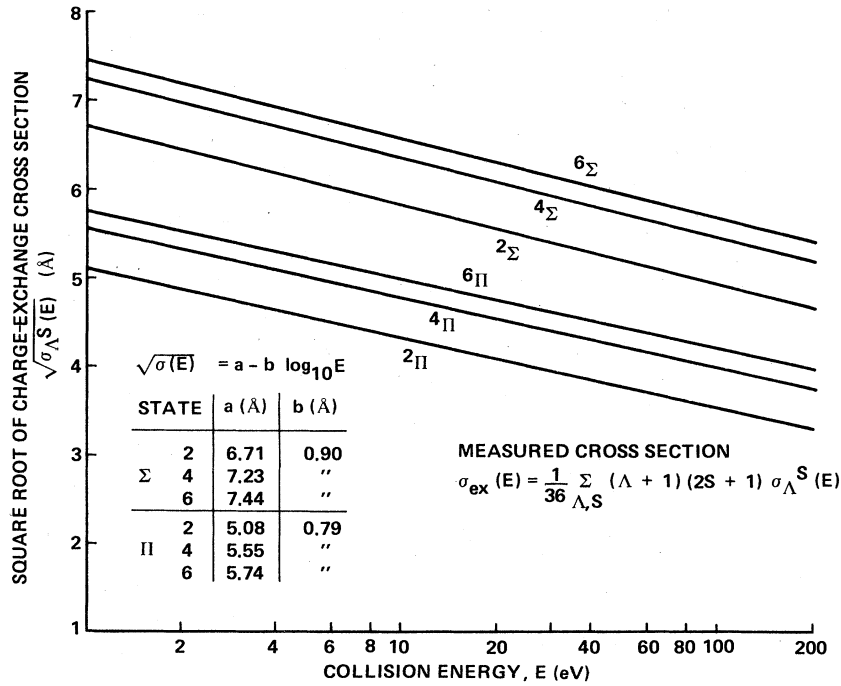


FIG. 2. N⁺-N charge-exchange cross section for specific values of the angular momentum.

those for each angular momentum (see Fig. 2). We compute this average from the curves of Fig. 2 and show the result in Fig. 3. In addition, we also include the contribution from the tail of the integration using an asymptotic approximation.¹⁰ Lastly, we plot the measured values from the beam experiment;⁴ according to the investigators, the error bars are mostly due to energy uncertainty, beam

spread, and fluctuations in the measurement of beam current.

We conclude that the calculated low-resolution cross section is in accord with the experiment. In addition, we note that the measured cross section presents structure which is outside the error bars. Likewise, we also expect that a more accurate calculation of the cross section would also yield

N⁺-N RESONANCE CHARGE TRANSFER

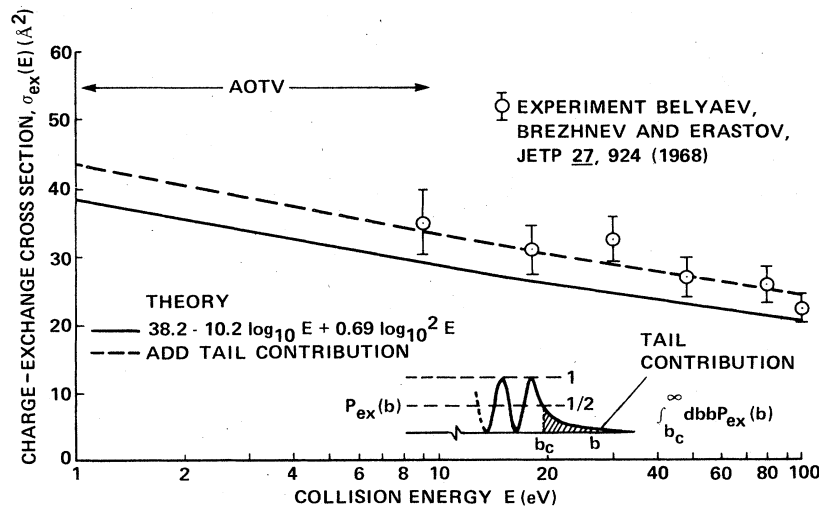


FIG. 3. N⁺-N charge-exchange cross section. The solid curve has been determined from relation (3); the contribution from the tail of the integration is added to this to obtain the dashed curve. The merged arrows cover the range of interest for AOTV applications.

structure. This structure is expected¹¹ to arise from the behavior of our calculated splitting at small R where we find curve-crossing-type interactions with excited-state-potential-energy curves. We are taking this into account in a more careful treatment of the small impact parameter contribution to the cross section. These results along with

transport properties that include the effects of the induced polarization forces, discussed above, at low collision energies will be reported later.¹²

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¹J. R. Stallcop, *J. Chem. Phys.* **54**, 2602 (1971).

²M. Capitelli and R. S. Devoto, *Phys. Fluids* **16**, 1835 (1973).

³M. Capitelli *et al.*, *Chem. Phys.* **19**, 269 (1977).

⁴V. A. Belyaev, B. G. Brezhnev, and E. M. Erastov, *Zh. Eksp. Teor. Fiz.* **54**, 1720 (1968) [*Sov. Phys. JETP* **27**, 924 (1968)].

⁵T. Dunning, Jr., *J. Chem. Phys.* **53**, 2853 (1970).

⁶J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. 1.

⁷C. Salez and A. Viellard, *Theor. Chim. Acta* **11**, 441 (1968).

⁸S. R. Langhoff, C. W. Bauschlicher, Jr., and D. P. Chong, *J.*

Chem. Phys. **78**, 5287 (1983).

⁹A. Dalgarno and H. N. Yadav, *Proc. Phys. Soc. London, Sect. A* **66**, 173 (1953); W. L. Fite, A. C. H. Smith, and R. F. Stebbings, *Proc. R. Soc. London, Ser. A* **268**, 527 (1962).

¹⁰A. Dalgarno, *Philos. Trans. R. Soc. of London, Ser. A* **250**, 426 (1958).

¹¹F. J. Smith, *Phys. Lett.* **20**, 271 (1966); J. Perel, R. H. Vernon, and H. L. Daley, *Phys. Rev.* **138**, 937A (1965).

¹²J. R. Stallcop and H. Partridge, in *Proceedings of the AIAA 20th Thermophysics Conference*, Williamsburg, VA, June 19–21, 1985.