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Ab initio potential curves and coupling-matrix elements for charge transfer from H to N^{2+} and N^{3+}

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Ab initio configuration-interaction methods are used to obtain the potential curves and coupling-matrix elements describing the charge transfer reactions $N^{2+}(^2P^o) + H \rightarrow N^+ + H^+$ and $N^{3+}(^1S) + H \rightarrow N^{2+} + H^+$. The basis sets are chosen to reproduce efficiently the crossing region and the polarization effects important for coupling-matrix elements. Correlation-energy problems are discussed in the context of rearrangement collisions and procedures are developed to minimize them. The computed reaction energies for the important channels of the reaction are within 7 and 1%, respectively, of the experimental values.

I. INTRODUCTION

That charge-transfer reactions of multiply charged ions with neutral H and He may play an important role in astrophysical plasmas has been recognized for some time.[1,2] The reactions will efficiently recombine the ions in regions where the fraction[4] of neutral H is as low as one part in 10.[3] Since hydrogen is effectively fully ionized by electron collisions at temperatures much larger than 50 000°K, the astrophysically interesting cross sections are those for collision energies of a few eV or less. Most of the recent theoretical[3,4] and experimental work[5] has been at much higher energies. At low energies, though experimental work is difficult, progress has been made using various theoretical techniques.[6] This work has been mainly limited to collisions where the electronic structure is that of a single electron outside of a closed shell. Here frozen core Hartree-Fock[7] or model potential[8] methods work reasonably well, though each has limitations even for these simple systems. Hartree-Fock (HF) methods naturally ignore whatever effects electron correlation will have, and model potential methods make no allowance for adjustments of the core electrons. When the core orbitals are frozen, the HF method is physically quite similar to the model potential technique in its treatment of the core electrons during the collision. Neither approach can be expected to treat satisfactorily charge-transfer reactions when more than one electron is actively involved. Most of the astrophysically important reactions are of this type. These involve multielectron open-shell configurations and/or excited core electrons and necessarily require more sophisticated treatment. By adapting to these multiply charged ion-atom collisions, the machinery which quantum chemists have developed for the study of molecular structure, all of the limitations of earlier methods can be overcome. The procedures and first results are presented in this paper.

At low energies the colliding ions form a quasimolecule whose electronic structure can be computed in the Born-Oppenheimer approximation. The shell structure of astrophysically interesting reactions poses no problem since very general open-shell calculations have been possible for some time and the effects of electron correlation can be approximately treated through configuration interaction. With carefully chosen basis sets the calculation of the potential surfaces to acceptable accuracy is feasible for all astrophysically interesting reactions (excluding those involving Fe). Of course, it is not necessary to compute all of them. Collisions of neutral H or He with ions of abundant species which are four or more times ionized usually have numerous open channels for charge transfer to highly excited Rydberg levels,[9] and other methods are more efficient for them. On the other hand, charge-transfer reactions involving doubly or triply ionized species usually involve the valence electrons or the first excited orbital out of the valence shell. Here quantum chemistry methods can be quite effective in determining the potential surfaces along which the charge-transfer reaction must proceed. Indeed, where the reaction involves a core excitation the use of configuration interaction (CI) is essential.[10]

This paper investigates the charge-transfer reactions

$$N^{2+}(2s^2\,2p,\ ^2P^o) + H \rightarrow N^+(2s\,2p^3,\ ^3D^o) + H^+, \quad (1)$$

$$N^{3+}(2s^2,\ ^1S) + H \rightarrow N^{2+}(2s^2\,3s,\ ^2S) + H^+, \quad (2a)$$

and

$$N^{3+}(2s^2,\ ^1S) + H \rightarrow N^{2+}(2s\,2p^2,\ ^2S) + H^+. \quad (2b)$$

Reactions (1) and (2a) are likely to be the dominant channels for charge-transfer processes.[7,9,11,12] Reactions (1) and (2b) are dielectronic processes: a 2*s* electron is promoted to 2*p* while the hydrogen 1*s* electron is transferred to a nitrogen II or III 2*p* orbital. Symmetry considerations imply that reaction (1) will proceed most rapidly for the $^3\Pi$ symmetry of the NH^{2+} quasimolecule. Reaction (2a) is a simple single-electron transfer outside a closed shell, and has been studied using frozen core Hartree-Fock,[7,12] as well as model potential[11] methods. The relevant molecular symmetry is $^2\Sigma^+$ for both (2a) and (2b).

Besides presenting the potential surfaces and matrix elements for the reactions, this paper will explore certain considerations of basis sets, molecular orbitals, and configurations which are important in defining a consistent method on which to base production calculations. The methods presented here will specifically treat reactions involving a neutral H atom and a first-row atom with a partially filled *L* shell which produce an atomic system either in an excited *L* shell or with an occupied lowest Rydberg orbital. These reactions are prototypes for charge transfer involving neutral H and doubly or triply ionized astrophysically abundant first-row atoms (C, N, O, and Ne). Extensions to He reactions will be presented in a later paper.

The results of earlier investigations[7,11,12] of reaction (2a) are in agreement for $T \geq 100$ K, but the rates differ by 50% at lower energies. Our calculations will test both the validity of the single-electron description of the transition and the applicability to charge transfer of the approximations based on it. Moreover, we will be able to determine the rate of a second open channel, reaction (2b), in the charge transfer. Earlier investigations[7,11,12] could not examine this state since transfer to it is a dielectronic process. While asymptotic analysis[8,13] would imply a small cross section, such considerations are inapplicable to dielectronic processes and may lead to erroneous results.[10] Configuration interaction using moderately large basis sets allows one to address all of these questions consistently.

All the computer programs are versions of earlier ones constructed at the California Institute of Technology and revised by Dr. S. Guberman for use on the local CDC 6400.

II. WAVE FUNCTIONS

A. General considerations

The electronic wave functions χ_n were expressed in terms of products of spherical harmonics and normalized Gaussian-type radial functions centered on each nucleus. The primitive basis sets are those of Huzinaga,[14] and contractions were made according to the rules developed by Dunning.[15] The main criterion for choosing the best basis set was the computed reaction energy, defined as the separation, ΔE_∞, of the initial and final potential curves at infinity. Because of the long range of the Coulomb repulsion in the final channel, in practice we compared the separations at $R = 10a_0$ and then corrected for the Coulomb repulsion.[16] The polarization energy of H in its incident channel is small and can be omitted from this comparison. We also define the quantity $\Delta_\infty \equiv [\Delta E_\infty - \Delta E)/\Delta E] \times 100$, which measures the deviation of ΔE_∞ from experiment as a percentage. The energy criterion is the most important, since the crossing distance R_x of the potential curves is given approximately for large R_x by equating the Coulomb repulsion to the experimental reaction energy ΔE:

$$R_x \approx Z_1 Z_2/\Delta E \ . \tag{3}$$

Thus an error in ΔE of *e* (defined via $\Delta E = \Delta E_\infty + e$) implies an error in R_x of $\Delta r \sim (eR_x/\Delta E)$. Asymptotic analysis of the interaction between the potential curves at the avoided crossing suggests[8,13] that

$$\Delta U \equiv E_2(R_x) - E_1(R_x) \sim R_x^2 \exp(-R_x) Ry \ .$$

Accordingly, an accurate calculation of the crossing distance R_x is crucial, and ΔE_∞ must be determined accurately. These formulas break down where molecular and polarization effects become important, but they are still useful criteria for gauging the quality of a basis set.

The viability of the basis set also requires a good estimate of the absolute energy of the potential curves and the inclusion of suitable polarization functions for the hydrogen 1*s* orbital and the outer shells of the $N^+(^3D^o)$ or $N^{2+}(^2S)$ ions. Polarization is important in the evaluation of the $\langle \psi_f | d/dR | \psi_i \rangle$ matrix element which couples the adiabatic eigenfunctions.[17] The derivative matrix element can be reduced to a combination of electric field matrix elements,[18] and because they are one-electron operators, they will be sensitive to polarization.

B. Polarization

The H-centered basis set and polarization functions are described elsewhere.[19] Only σ polarization functions were added to the H basis since tests showed that π polarization functions had a negligible effect on the energy and modified the matrix elements by less than 10%, while substantially increasing the computer time.

To describe the polarization of the $N^+(^3D^o)$ ion

TABLE I. $^3\Pi$ structure of NH^{2+}.

Separated atoms	Molecular state[a]	Configuration (CPD)	ΔE (eV)	ΔE_∞ (eV)	Δ_∞ (%)	R_x (a_0)
$N^+(2s^2 2p^2, {}^3P)$ + H^+	$1^3\Pi$	$2\sigma^2 3\sigma 1\pi_y$	16.01	15.75	−1.7	1.7
$N^+(2s2p^3, {}^3D^0)$ + H^+	$2^3\Pi$	$2\sigma 3\sigma^2 1\pi_y$	4.57	4.22	−7.6	5.9
$N^+(2s2p^3, {}^3P^0)$ + H^+	$4^3\Pi$	$2\sigma 1\pi_x^2 1\pi_y$	2.46	1.90	−22.8	11.0
$N^{2+}(2s^2 2p, {}^2P^0)$ + $H({}^2S)$	$3^3\Pi$	$2\sigma^2 4\sigma 1\pi_y$	0.00	0.00	···	···

[a] Numbered according to computed order at $R = 10.0a_0$.

by H^+, we added $3d\sigma$ and $3d\pi$ basis functions, represented by a contraction of two primitive Gaussians,[20] with an effective Slater exponent of 2.141. The $3d_{x^2} + 3d_{y^2} + 3d_{z^2}$ was excluded. The value 2.141 is the average Slater exponent ζ_{eff} of the $2p$ functions of the $N^+({}^3D^o)$ ion, determined from atomic Slater calculations,[21] and defined by

$$\zeta^s_{\text{eff}} \equiv \sum_i \zeta^s_i C_i \Big/ \sum_i C_i , \qquad (4)$$

where ζ^s_i are the Slater exponents and C_i are the expansion coefficients of the atomic orbital.

Calculations[22] for other ions showed that this prescription approximated reasonably the exponent determined by optimization of the long-range polarization energies. For reactions (2a) and (2b) an effective Slater-type orbital (STO) exponent for the $3d$ contracted Gaussian-type orbital (GTO) of 2.3514 was obtained from the $2p$ orbital[21] in N^{2+} $(2s^2 2p, {}^2P^o)$. The polarization of the Rydberg level of $N^{2+}(2s^2 3s, {}^2S)$ was treated by including diffuse p basis functions described later.

C. Configurations

Consider reaction (1), whose relevant $^3\Pi$ molecular states are shown in Table I, together with their separated atom limit, molecular configuration and formal crossing distances computed by use of (3). Similar information for reactions (2a) and (2b) is in Table II. The interesting transition $3\,{}^3\Pi \rightarrow 2\,{}^3\Pi$ is a two-electron process involving a core excitation, and configuration interaction must be used in order to obtain useful results. In the $3\,{}^3\Pi$ state one electron is well separated from the others so that the $3\,{}^3\Pi$ state has a much smaller correlation energy than does the $2\,{}^3\Pi$ state.

Suppose our basis set is well balanced and recovers a certain fraction, say x, of the L-shell correlation energy[23] of each state. Then if the two states differ by ΔC in their L-shell correlation energies, our calculation will contain an asymptotic error in the reaction energy of $(1-x)\Delta C$. Numerous test atomic Hartree-Fock calculations[22] show that contracted Gaussian basis sets[24] which do not bias substantially either reaction ion N^+ or N^{2+}, with respect to the Hartree-Fock limit, can be easily devised. Thus all of the difference between the computed and experimental reaction energies can be traced to correlation effects.

Thus the success of *ab initio* methods in treating charge transfer processes with hydrogen depends, with a few exceptions, on a proper treatment of

TABLE II. $^2\Sigma^+$ structure of NH^{3+}.

Separated atoms	Molecular state[a]	Configuration (CPD)	ΔE (eV)	ΔE_∞ (eV)	Δ_∞ (%)	R_x (a_0)
$N^{2+}(2s^2 2p, {}^2P^0)$ + H^+	$1\,{}^2\Sigma^+$	$2\sigma^2 3\sigma$	33.83	33.56	−0.8	1.6
$N^{2+}(2s2p^2, {}^2D)$ + H^+	$2\,{}^2\Sigma^+$	$2\sigma 3\sigma^2$ $2\sigma 1\pi_x^2$	21.30	20.83	−2.2	2.6
$N^{2+}(2s2p^2, {}^2S)$ + H^+	$3\,{}^2\Sigma^+$	$2\sigma 1\pi_y^2$	17.59	16.81	−4.4	3.1
$N^{2+}(2s^2 3s, {}^2S)$ + H^+	$4\,{}^2\Sigma^+$	$2\sigma^2 4\sigma$	6.39	6.32	−1.1	8.5
$N^{2+}(2p^3, {}^2P^0)$ + H^+	$6\,{}^2\Sigma^+$		5.26	4.36	−17.1	10.3
$N^{2+}(2s^2 3p, {}^2P^0)$ + H^+	$7\,{}^2\Sigma^+$		3.37	3.11	−7.7	16.1
$N^{2+}(2s^2 3d, {}^2D)$ + H^+	···		0.70	···	···	76.9
$N^{3+}(2s^2, {}^1S)$ + $H({}^2S)$	$5\,{}^2\Sigma^+$	$2\sigma^2 5\sigma$	0.00	0.00	···	···

[a] See footnote for Table I.

the correlation energy. To describe the dissociation of a molecule, it is important to treat all of the configurations for proper dissociation[25] (CPD) equally in the CI calculation. For charge transfer at least two molecular states are equally important, and often the problem requires several additional states. To obtain a balanced CI wave function for each we included all single and double excitations (within an orbital space defined below) out of the CPD of each interesting channel. Inclusion of triple excitations while enormously increasing the cost made only insignificant improvements,[22] and was judged not worthwhile. Moreover, in all cases the core 1σ orbitals of the heavy ion were unexcited and remained doubly occupied. The CPD of each channel are listed in Tables I and II.

D. Basis sets; orbital space

The main components of the molecular eigenstates which describe reactions (1), (2a), and (2b) is the set of Gaussian basis functions centered on the N nucleus. We considered several sets of contracted Gaussian-type orbitals (GTO) in an effort to optimize our descriptions of the reactions within the constraints described above. The core $1\sigma^2$ and the L-shell electrons of NH^{2+} and NH^{3+} could be described by either the $(9s5p)$ or $(10s6p)$ primitive sets of Huzinaga.[14] The question of which primitive set is better suited, and the important related question of the most efficient contraction for the set have been mainly investigated in the context of reaction (1), as described in detail below. The related, but distinct, problem of determining an acceptable orbital space in which to perform the CI calculation is also addressed in Secs. IID1 and IID2.

1. NH^{2+}

The test calculations utilized the $(9s5p)$ primitive set contracted to $[3s2p]$, $[4s3p]$, and $[5s4p]$, and the $(10s6p)$ primitive set contracted to $[5s4p]$. For all cases the H-centered functions were identical, but for two cases the $3d$ polarization set was varied.[26] For all of these trials Hartree-Fock wave functions, which correctly describe the dissociation of the N-electron $1\,^3\Pi$ molecular spin multiplet, were computed at $R=10a_0$. Virtual orbitals, appropriate to motion in the field of $N-1$ electrons occupying the frozen orbital HF ground-state system, were obtained with the improved virtual orbital[27] (IVO) method. In all cases the excited 4σ orbital closely resembled a 1s orbital centered on the H nucleus. Except for the $[3s2p]$ calculation, the σ orbital with the highest energy was deleted from the orbital space. From its structure the orbital was clearly important only for correlating the $1\sigma^2$ electrons. Since the 1σ was always kept doubly occupied, we deleted the highest σ orbital. Tests verified that it was unimportant. Then these virtual orbitals together with the Hartree-Fock orbitals comprised the orbital space for the CI calculations.

Table III summarizes the results of the trials. As discussed in Sec. IIA the most significant measure of adequacy of the basis sets is ΔE_∞ for the $2\,^3\Pi$ state, which is used to obtain Δ_∞, the percentage error in the reaction energy relative to

TABLE III. NH^{2+}, Π^3: Basis sets and computed energies for $R=10a_0$.

State	Primitive set: Contracted set: Entry	(9s5p) $[3s2p]$ [c]	$[4s3p]$ [c]	$[5s4p]$	(10s6p) $[5s4p]$	Expt. ΔE (eV)
$1^3\Pi$	E [a] (a.u.)	−53.8173	−53.848 25	−53.855 34	−53.861 77	
	ΔE_∞ [b] (eV)	15.15	15.68	15.75	15.75	16.01
	Δ_∞ (%)	−5.4	−2.1	−1.6	−1.7	
$2^3\Pi$	E	−53.3825	−53.423 68	−53.431 80	−53.437 45	
	ΔE_∞	3.32	4.12	4.22	4.20	4.57
	Δ_∞	−27.4	−9.8	−7.6	−8.1	
$3^3\Pi$ [d]	E	−53.3604	−53.372 19	−53.376 62	−53.383 13	
	ΔE_∞	...	...	...	...	...
	Δ_∞	...	...	...	...	
$4^3\Pi$	E	−53.3145	−53.341 19	−53.346 37	−53.352 59	
	ΔE_∞	1.47	1.88	1.90	1.89	2.46
	Δ_∞	−40.24	−23.7	−22.9	−23.2	

[a] Computed energy (a.u.) at $R=10a_0$.
[b] See Ref. 16.
[c] See Ref. 26.
[d] Entrance channel $N^{2+}+H$.

experiment. The [$3s2p$] set is clearly inadequate since $\Delta_\infty(2\,^3\Pi)$ is about 27%. In fact this set places the avoided crossing near $R=8.25a_0$, a full $2a_0$ larger than the value indicated by the experimental separated atom energy limits. The [$4s3p$] set is less contracted, and its additional flexibility allows the CI calculation to recover a large fraction of the L-shell correlation energy. Most of the improvement occurred in the N^+ ion, as expected, and Δ_∞ shrank to 9.8%. Still less contracted is the [$5s4p$] set derived from the ($9s5p$) primitive set. ΔE_∞ improved by 0.1 eV and Δ_∞ was reduced to 7.6%. The improvement, though, is much less than for the change from [$3s2p$]$\rightarrow$[$4s3p$], indicating slow convergence for enlargements of the [$4s3p$] set. Since the number of configurations is rapidly increasing with basis set size, diminishing returns forces one to examine the increased accuracy of an enlarged basis set in light of its larger computer time requirements. For NH^{2+} the improvement of Δ_∞ from -9.8% to -7.6% seemed worthwhile, so we adopted the [$5s4p$] basis set contracted from the ($9s5p$) primitive set. We also tested the [$5s4p$] basis contracted from the ($10s6p$) primitive set. The results in Table III show that it is inferior with respect to ΔE_∞, though its absolute energy is lower. This occurs because the ($10s6p$) set produces a better description of the $1\sigma^2$ core electrons, which, however, do not participate in the reaction. In fact, in tests[22] with a ($10s6p$)$\rightarrow$[$5s4p$] basis for other ions, it performed worse, measured in terms of ΔE_∞ in all cases. Accordingly all our calculations use the ($9s5p$) primitive set, contracted to optimize ΔE_∞ subject to computer time constraints.

The [$5s4p$] set allows the very tight s-type basis functions more flexibility, so that in fact the two highest energy σ orbitals will correlate mainly the $1\sigma^2$ core electrons. Accordingly, we deleted both of them (instead of just the highest). Tests verified their unimportance both in terms of energy and in terms of occupation number. Then our total basis set was [$5s4p1d/2s2p_z$] contracted from ($9s5p2d/4s3p_z$), and the resulting orbital space contained twelve σ, five π_x, and five π_y orbitals, for a total of 22. Excitations into this space from the CPD with $1\sigma^2$ fixed resulted in 502 spatial configurations (SPC) and 1048 spin eigenfunctions (SEF). For the production work we used this configuration set and orbitals derived from the NH^{2+}, $1\,^5\Sigma^-$ state, whose separated atom limit is $N^+(2s2p^3,\,^5S^o)+H^+$. At $R=10a_0$ these orbitals produced results insignificantly better than orbitals derived from the $1\,^3\Pi$ state, but had the desirable feature that the π_x and π_y orbitals were equal and computed simultaneously. In addition to being simpler to handle in terms of the mechanics of the calculation, such orbitals from high-spin states can better span the basis set space since they are more separated spatially.[28] The results of the production work are presented in Sec. III.

2. NH^{3+}

Previous work[7,11,12] showed that charge transfer from H to N^{3+} is probably dominated by a transition to the $N^{2+}(2s^2 3s,\,^2S)$ state. However, one cannot *a priori* rule out a significant contribution from transitions to $N^{2+}(2s2p^2,\,^2D)$ and $N^{2+}(2s2p^2,\,^2S)$ since it has been shown[10] that close avoided crossings can exist even at small R for dielectronic transitions. An *ab initio* calculation of the rate for any charge-transfer process must include all possible important channels in order to be consistent and to treat correctly any interference effects which might occur in the scattering solution. The question of when the transition probability becomes small as R_x becomes small has not been addressed for dielectronic transitions, though single-electron processes become inefficient[9] for $R_x \lesssim 7a_0$. The $N^{2+}(2s2p^2,\,^2S)$ potential has a crossing near $3a_0$ (see Table II), somewhat less than the crossing at $\sim 4a_0$ noted[10] for O^{2+}+H. Accordingly, it was deemed important to investigate charge transfer to both $N^{2+}(2s2p^2,\,^2S)$ and the closely related state $N^{2+}(2s2p^2,\,^2D)$. Charge transfer to $N^{2+}(2s^2 3p,\,^2P^o)$ can be shown to be unimportant through asymptotic arguments.[11] Calculations of dielectronic charge transfers for $O^{2+}+H$ (Ref. 10) and $N^{2+}+H$ (this paper) suggest that the three-electron process of $N^{3+}+H\rightarrow N^{2+}(2p^3,\,^2P^o)+H^+$ is unimportant since its crossing is large for a multielectron reaction. The CPD which result from concentrating on the potentially important states are listed in Table II.

A basis to describe the $2\,^2\Sigma^+$ and $3\,^2\Sigma^+$ states as well as the entrance channel $N^{3+}+H$ was constructed by first contracting the ($9s5p$) primitive set to a [$4s3p$] set. A $3d$ polarization function ($2d$)$\rightarrow$[$1d$] with an effective Slater-type exponent equal to 2.3514 (obtained from the p orbital of N^{2+}, $^2P^o$) and the H-centered basis functions were added. Proper description of the important $4\,^2\Sigma^+$ channel which dissociates to $N^{2+}(2s^2 3s,\,^2S)+H^+$ requires one to augment the standard valence basis set with diffuse functions. We added three s-type Gaussians with exponents 0.104 71, 0.035 48, and 0.012 59 as determined by extrapolation[29] of the nearly geometric progression of the ($9s$) primitive basis. No attempt at optimization was made, nor needed as our results will show. To polarize these functions we added two diffuse $2p\sigma$-type Gaussian primitives determined from extrapolation of the ($5p$) primitive basis. The exponents used were 0.048 98 and 0.009 120. Since the Rydberg orbital of interest (4σ in Table II) has the $3s$ level of N^{2+} as an atomic limit no diffuse $2p\pi$, nor $3d$ polarization functions were added.[30] The basis set is designated $[7s5p_z3p_{xy}1d/2s2p_z]$.

The orbital space was generated from HF and IVO calculations of the ground $1\,^2\Sigma^+$ state as described for NH^{2+}. The $1\sigma^2$ core was kept doubly occupied and the highest σ orbital which correlates the pair was discarded, reducing the orbital space to 24 orbitals (sixteen σ, four π_x, and four π_y). The configuration space created by including all single and double excitations out of the CPD into this orbital space contained 558 SPC and 962 SEF.

The results of the CI calculations with the $[7s5p_z3p_{xy}1d/2s2p_z]$ basis set are listed in Table II. Clearly the calculation was very successful in reproducing relative separations of the important $2\,^2\Sigma^+$, $3\,^2\Sigma^+$, and $4\,^2\Sigma^+$ states from the $5\,^2\Sigma^+$. The key diagnostic Δ_∞ is -2.2, -4.4, and -1.1%, respectively. Such a small Δ_∞ implies that calculations with the basis set will nicely reproduce the crossing structure suggested by the experimental energy levels. The error in ΔE_∞ for $2\,^2\Sigma^+$ is 0.47 eV, essentially the same as the $[4s3p1d/2s2p_z]$ basis produced for the $2\,^3\Pi$ state of NH^{2+}. However, for NH^{3+}, the analogous extension to a $[5s4p]$ contraction of $(9s5p)$ did not produce substantially improved results. The error for the $6\,^2\Sigma^+$ and $7\,^2\Sigma^+$ states is large since their main configurations were not included as CPD. These results justify our simple procedure for obtaining the diffuse exponents, as well as the validity of the orbital and configuration generation procedure for treating charge transfer to Rydberg levels. Moreover, the procedures were successful in obtaining good relative asymptotic energy levels for a dielectronic process. In absolute terms the $5\,^2\Sigma^+$-$4\,^2\Sigma^+$ reaction energy ΔE_∞ is only 0.07 eV smaller than the experimental value. One should not, however, consider such small differences "errors," since many small terms are left out of the calculation of ΔE_∞. One such term is the polarization attraction in the $N^{3+}+H$ channel, whose value at $R=10a_0$, 0.055 eV, accounts for nearly all of what we term error. Of course differences on the order of a few tenths of an eV are real, such as the 0.47 eV error for ΔE_∞ of the $2\,^2\Sigma^+$ state. Here, though, the interesting range of internuclear distances is $3-4a_0$, where molecular effects are important, and we can expect the large $[7s5p_z3p_{xy}1d/2s2p_z]$ basis set to do well since the

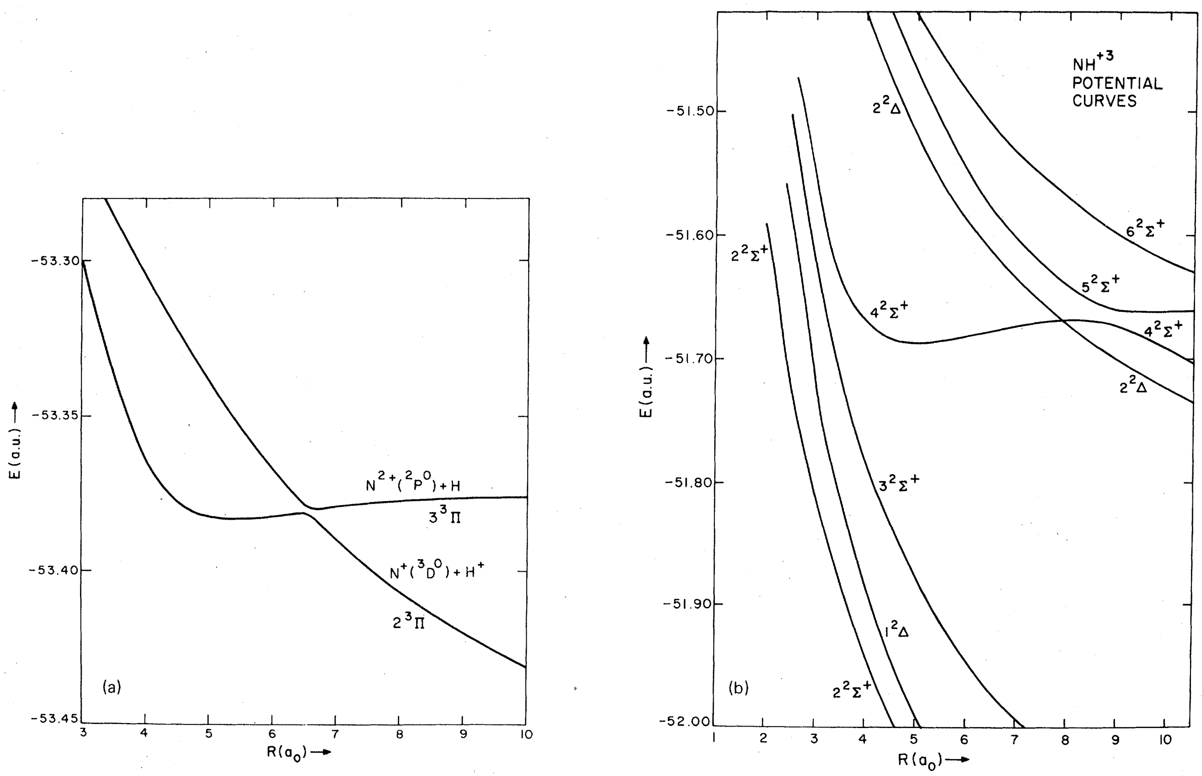

FIG. 1. (a). Potential surfaces of NH^{2+}, $^3\Pi$, relevant to reaction (1). The states are labeled according to their asymptotic limits given in Table I. (b) Potential surfaces of NH^{3+}, $^2\Sigma^+$, relevant to reactions (2a) and (2b). The states are labeled according to their asymptotic limits given in Table II.

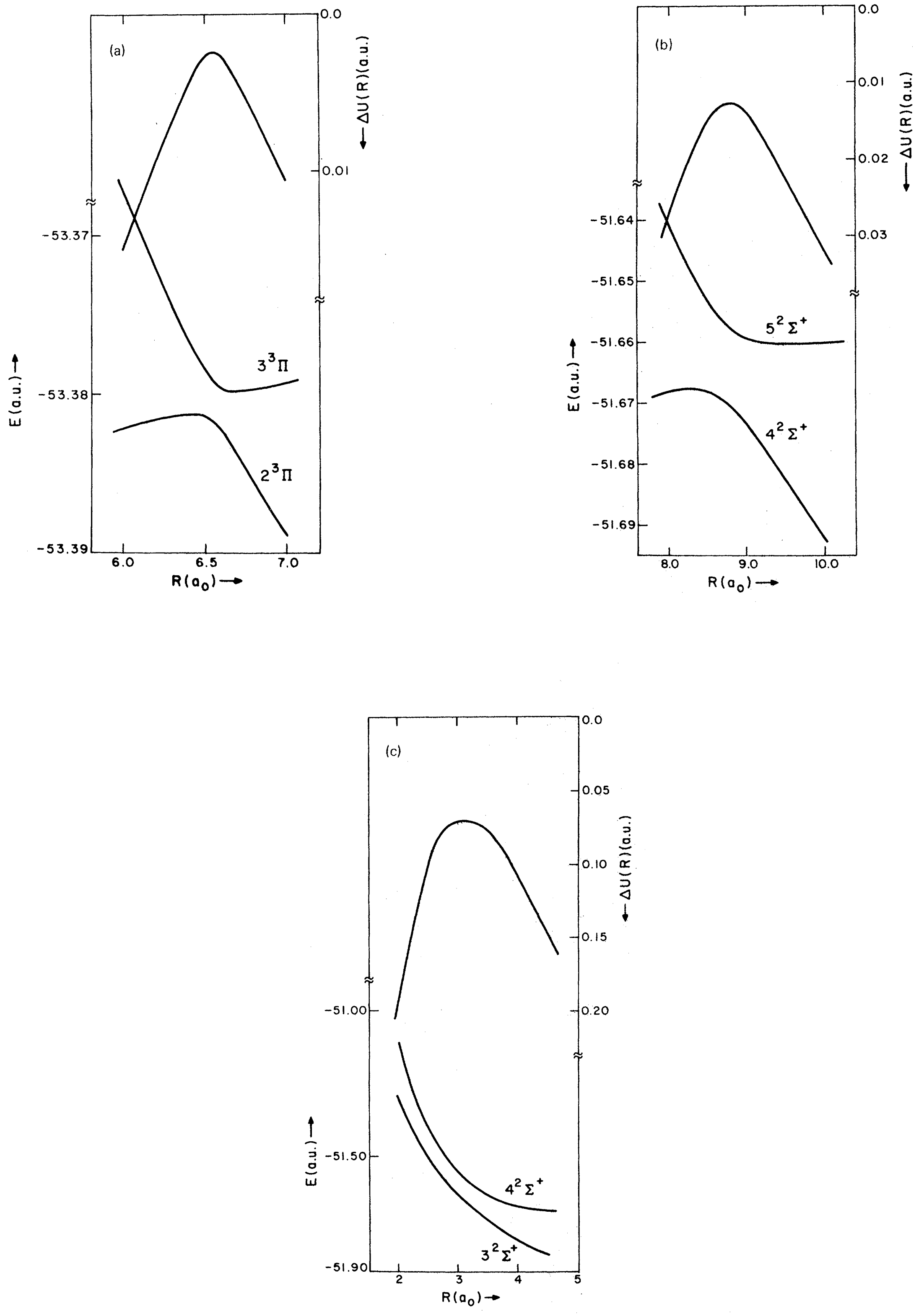

FIG. 2. (a) The potential curves and their difference near the avoided crossing important for reaction (1). (b) The potential curves and their difference near the avoided crossing important for reaction (2a). (c) The potential curves and their difference near the avoided crossing important for reaction (2b).

most diffuse valence primitives are not contracted. This was the basis set for the NH^{3+} production work described in Sec. III.

III. RESULTS

Figures 1(a) and 1(b) show the potential surfaces for the NH^{2+}, $^3\Pi$ and NH^{3+}, $^2\Sigma^+$ states, respectively, obtained through application of the basis sets and procedures described above to calculations at a large number of internuclear distances from 2 to $10a_0$. The point spacing is mainly $0.5a_0$, except near avoided crossings where the spacing was reduced to whatever was required to delineate the large curvature of the surfaces. For NH^{3+} some $^2\Delta$ states were also obtained since the calculation for the $^2\Sigma^+$ states was done in the A_1 symmetry of the C_{2v} point group. These are not well described and do not play a role in charge transfer, but we include them in Fig. 1(b) for completeness. The regions near the avoided crossings are shown in detail in Figs. 2(a), 2(b), and 2(c), together with $\Delta U(R)$, the difference between the two interacting potential curves. The point of closest approach is R_x, the "crossing" distance in the two-state Landau-Zener model.[31] It is the quantity $\Delta U(R_x)$ which is required for application of the Landau-Zener formula to determine the transition probability for a collision. For the avoided crossing of the states $2\,^3\Pi$ and $3\,^3\Pi$ of NH^{2+} shown in Fig. 2(a), $R_x = 6.55a_0$ and $U(R_x) = 0.0024$ a.u. $= 0.0653$ eV. This is more than an order of magnitude smaller than an asymptotic analysis[8,13] using $\Delta U(R) \sim 13.6R^2 \exp(-R)$ (eV) would predict, and further emphasizes the qualitative distinction between simple single-electron charge-transfer processes and dielectronic processes, first pointed out[10] for $O^{2+} + H$. The Landau-Zener formula predicts the rate coefficient at 10^4K for (1) to be 5×10^{-10} $cm^3\,sec^{-1}$.

The interaction of the $5\,^2\Sigma^+$ and $4\,^2\Sigma^+$ state of NH^{3+} is shown in Fig. 2(b). For this single-electron process, $R_x = 8.8a_0$ and $\Delta U(R_x) = 0.344$ eV, in excellent agreement with model potential[11] and Hartree-Fock[7] results as well as asymptotic analysis.[8,13] The same collision of N^{3+} with H also has a dielectronic open channel for charge transfer, $4\,^2\Sigma^+ \rightarrow 3\,^2\Sigma^+$, and the avoided crossing is shown in Fig. 2(c). Note that interior to $R = 8.8a_0$ the $4\,^2\Sigma^+$ state of NH^{3+} takes on the character of the $N^{3+} + H$ channel, so that the $4\,^2\Sigma^+ - 3\,^2\Sigma^+$ interaction describes charge transfer. The avoided crossing occurs at $R_x = 3.1a_0$ and $\Delta U(R_x) = 0.071$ a.u. $= 1.93$ eV. As expected, it is much smaller than predicted for a single-electron process.[8,13] The $2\,^2\Sigma^+$ state may also play a role in this interaction. The $2\,^2\Sigma^+$ eigenvector shows that some of the $N^{3+} + H$ character leaks into it. Moreover, since $2\,^2\Sigma^+$ and $3\,^2\Sigma^+$ are, for the most part, different linear combinations of the same spin eigenfunctions (those of $2\sigma 3\sigma^2$, $2\sigma 1\pi_x^2$, and $2\sigma 1\pi_y^2$) one might expect that both states would need to be included in a quantal scattering solution. This point will be discussed in detail later. The Landau-Zener formula suggests the reaction rate 3×10^{-9} $cm^3\,sec^{-1}$ at 10^4 K for formula (2a). For reaction (2b) a much smaller rate is predicted, but since the formula is unreliable when $\Delta U \lesssim KT$, quantal calculations are needed to assess accurately the importance of (2b).

For collisional charge transfer the operator which induces the transition is $1/i\,\vec{\nabla}_R$, the nuclear momentum operator, where R is the internuclear distance. Since all of the transitions in which we are interested have $\Delta\Lambda = 0$, where Λ is the component of the electronic angular momentum along the internuclear axis, the relevant transition-matrix elements are $\langle \psi_f | d/dR | \psi_i \rangle$. An operator transformation[18] reduces this formidable integral to a simpler one involving the electric field operator which can be easily evaluated with the configuration interaction wave functions. For eigenstates of the electronic Hamiltonian ψ_i, ψ_f whose energies are E_i, E_f, the identity

$$\left\langle \psi_f \left| \frac{d}{dR} \right| \psi_i \right\rangle = (E_i - E_f)^{-1} \left\langle \psi_f \left| \frac{dV_{ne}}{dR} \right| \psi_i \right\rangle \tag{5}$$

holds, where V_{ne} is the electronic-nuclear interaction.[18(a)] For the reactions considered here,

$$\frac{dV_{ne}}{dR} = -\sum_{i=1}^{n} \left(\frac{(1-\eta) Z_N z_{iN}}{r_{iN}^3} - \frac{\eta Z_H z_{iH}}{r_{iH}^3} \right), \tag{6}$$

where Z_N and Z_H are the nuclear charges of N and H located at $\vec{R}_N$ and $\vec{R}_H$, respectively.[18(b)] Also, $R = |\vec{R}_N - \vec{R}_H|$, $r_{iA} = |\vec{r}_i - \vec{R}_A|$, for electron i, and the internuclear axis is the $\hat{Z}$ axis. The derivative is taken keeping the electronic coordinates $\vec{r}$ fixed with respect to the body-fixed origin $\vec{R}_0 = \eta\vec{R}_N + (1-\eta)\vec{R}_H$. Unless $\vec{R}_0 = \vec{C}_m$, the center of mass of the nuclei, and thus $\eta = M_N/(M_N + M_H)$ for nuclear masses M_N, M_H, couplings between the electronic and nuclear motion besides (5) arise which seriously complicate the coupled equations.[32]

Besides tractability, the new expression allows one to partition the coupling into a factor which depends on the character of the avoided crossing and a factor which *smoothly* varies through the avoided crossing, even though the wave functions and potential curves change abruptly.[18(b)] This greatly eases interpolation problems near the crossing region where $\langle \psi_f | d/dR | \psi_i \rangle$ varies rapidly. Though the identity (5) is strictly valid only if ψ_i and ψ_f are exact eigenstates, many properties of the expression and the resultant coupling matrix elements suggest that it provides useful

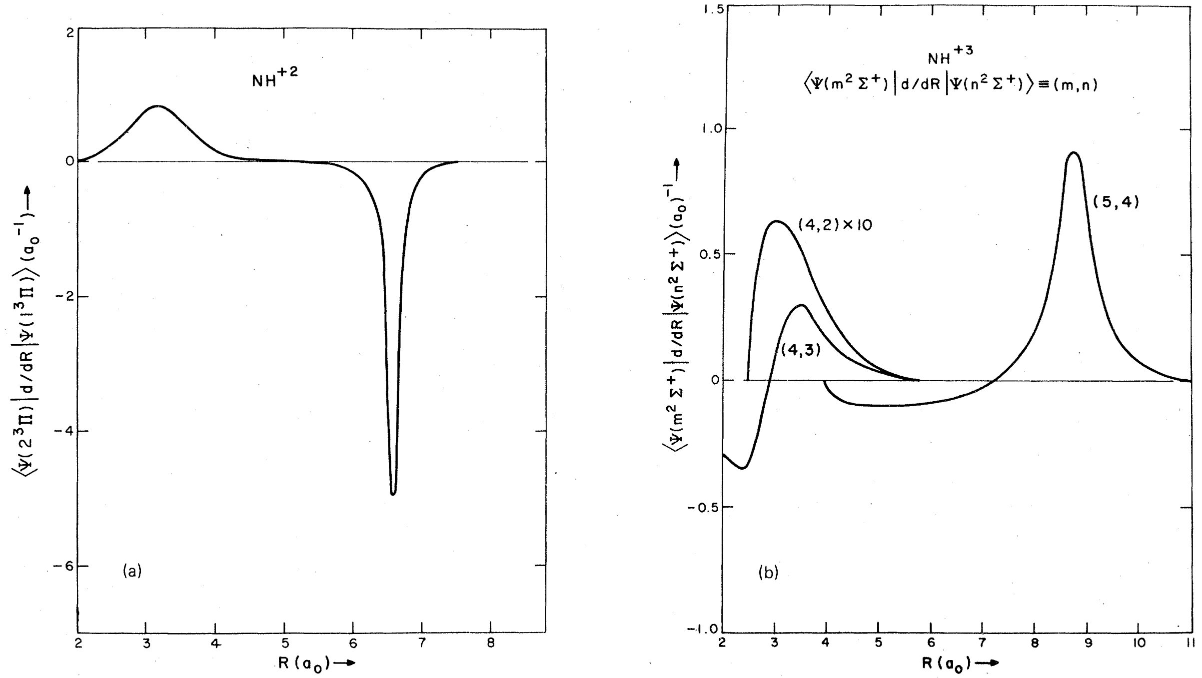

FIG. 3. (a) Radial coupling-matrix elements for reaction (1). (b) Radial coupling-matrix elements for reactions (2a) and (2b).

results for charge-transfer reactions.[18(b)]

The large peak in the coupling element near $6.55a_0$ in Fig. 3(a) coincides with the avoided crossing of the $2\,^3\Pi$ and $3\,^3\Pi$ potential curves of NH^{2+}, and is the primary agent inducing reaction (1). The coupling is very large at the peak, $\approx 5a_0^{-1}$, but having a full width at half intensity of only $0.2a_0$, is very localized. Unexpectedly, there is a second peak in the coupling elements near $R = 3a_0$, where a second avoided crossing exists. Examination of the CI wave vectors showed that large changes in the CI coefficients occur there, and indeed bears out the existence of the second crossing. Such secondary crossings at small R are probably difficult to predict, and illustrate that some important effects might be overlooked if attention is focused only on the primary crossing region, near $6.55a_0$ in this case.

The NH^{3+} coupling-matrix elements important for reactions (2a) and (2b) are shown in Fig. 3(b). The complicated structure is most easily analyzed in reference to the potential curves. Following the notation indicated in the figure, the (5,4) peak near $8.8a_0$ corresponds to the avoided crossing of $5\,^2\Sigma^+$ and $4\,^2\Sigma^+$ there. Interior to this, the N^{3+}+ H character is associated with the $4\,^2\Sigma^+$ state so that its matrix elements induce charge transfer here. Near $3a_0$ the (4,3) and (4,2) transition elements both peak, suggesting that the avoided crossing shown in Fig. 2(c) in fact is a three-state interaction. Most of the interaction is between $4\,^2\Sigma^+$ and $3\,^2\Sigma^+$, but the $2\,^2\Sigma^+$ must also play a role, as the (4,2) matrix element shows.

The (3,2) coupling element, not shown, describes the atomic transition N^{2+}($2s2p^2$, ^2D) → N^{2+}($2s2p^2$, ^2S) induced by proton impact. It is small and featureless throughout the calculated range. Similar couplings exist for many proton collision, which we will discuss elsewhere.

The coupling matrix elements involving the $5\,^2\Sigma^+$ are not shown for $R \lesssim 4a_0$. Interior to this point the $5\,^2\Sigma^+$ undergoes several character changes due to avoided crossings with high-lying states whose CPD were not included in the reference set. Consequently, $5\,^2\Sigma^+$ is not accurately treated at small internuclear separations. Along the $5\,^2\Sigma^+$ potential, penetration to small distances requires energies of about 10 eV, implying that low-energy charge transfer will not be strongly affected by these higher states. In any case the role of these states can be examined during the course of quantal scattering calculations.

IV. SUMMARY

These calculations have demonstrated the feasibility of computing the potential surfaces and coupling-matrix elements relevant to charge-transfer processes via the methods of quantum chemistry. That all of the states potentially important in the reaction have been included and treated uniformly for all internuclear distances will allow one to utilize the results in a quantal scattering solution without unduly restricting the number of channels of the interaction regime. Such considerations are clearly important, especially in view of the complicated multichannel phenomena in NH^{3+} and the secondary crossing in NH^{2+}. The inclusion of configuration effects in such a way as to avoid biasing any particular channel greatly enlarges the range of processes which can be studied quantitatively. This paper has mapped out in detail procedures which allow the computation of potential surfaces and matrix elements of reasonably uniform quality over the whole collision surface, which are sufficiently accurate for most astrophysically relevant charge-transfer processes.

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