

## Interactions of H and H<sup>-</sup> with He and Ne

R. E. Olson

*Molecular Physics Laboratory, SRI International, Menlo Park, California 94025*

B. Liu

*IBM Research Laboratory, 5600 Cottle Road, San Jose, California 95193*

(Received 19 May 1980)

Potential energies have been computed for the ground states of HeH, HeH<sup>-</sup>, NeH, and NeH<sup>-</sup> using the configuration-interaction method. The HeH<sup>-</sup> potential curve is found to cross into the HeH continuum at  $R = 2.70a_0$  with a threshold energy of 1.34 eV. In contrast, the NeH<sup>-</sup> state is found only to merge with the NeH continuum at  $R \approx 2.25a_0$  at an energy of 2.7 eV. These calculations suggest the threshold-energy collisional electron detachment for HeH<sup>-</sup> can be best described by the complex potential method, while the NeH<sup>-</sup> detachment mechanism is more akin to a charge transfer to the continuum process.

### I. INTRODUCTION

The determination of the collision mechanisms responsible for electron detachment in low-energy collisions of negative ions with atoms is an interesting and active field. Two different collision mechanisms have been proposed to explain the experimental collision data. One is the complex potential method given by Lam *et al.*<sup>1</sup> which requires a deep penetration of the negative-ion state into the continuum for applicability. This electron-detachment model is similar to that first used by Mason and Vanderslice<sup>2,3</sup> with the extension that the transition probabilities are computed in a manner similar to that employed in Penning ionization calculations. Another mechanism, termed the "zero-radius model," is similar to a charge transfer to the continuum process which only requires the negative-ion and neutral states to merge reasonably close to one another. Calculations using this latter mechanism have been presented by Gauyacq<sup>4</sup> using an extension of the formalism previously given by Devdariani.<sup>5</sup>

It has not been possible to rigorously test the proposed mechanisms against experimental data because of the lack of the most basic input information, the potential-energy curves. Previous potential-energy calculations,<sup>6</sup> which address this collision problem, were at the self-consistent-field (SCF) level and the resultant energies require considerable shifts to achieve the correct asymptotic energy separations between the neutral and ionic-potential curves. Hence, questions remain as to the reliability of the SCF calculations.

In this paper, we present accurate configuration-interaction (CI) potential-energy curves for the ground negative-ion and neutral states of HeH and NeH. These systems were chosen because there are only a small number of electrons, thus allowing an accurate determination of the interaction

energies. Another reason for the choice is that the experimental data indicate quite different total and differential cross-section behavior for the two systems, leading us to expect some difference in the relations between the negative-ion and neutral potential-energy curves. Hence, these calculations should shed some light on the various collision mechanisms for electron detachment.

### II. CALCULATIONAL METHOD

Approximations to the Born-Oppenheimer electronic wave functions and energies were calculated using the self-consistent-field (SCF) and configuration-interaction (CI) methods. An electronic wave function was expanded in an orthonormal  $n$ -particle basis set of  $C_{\infty v}$  symmetry and equivalence-restricted configuration state functions (CSF). These CSF's were linear combinations of Slater determinants such that each had the symmetry and multiplicity of the molecular state under consideration. The Slater determinants were constructed from an orthonormal set of orbitals which were expanded in terms of an elementary basis set of Slater-type functions centered at the atomic nuclei. The calculations were performed using *ALCHEMY*, a system of programs for the calculations of molecular wave functions developed at IBM by Bagus, Liu, McLean, and Yoshimine.

The Slater-type function basis sets employed in the HeH and NeH calculations are given in Table I. The  $(5s/3p/2d)$  basis for H is the same as used previously<sup>6</sup> and yields the exact energy for H to six decimal places and a dipole polarizability of  $4.4993a_0^3$ , very close to the exact value of  $4.5000a_0^3$ . The CI energy computed for H<sup>-</sup> is  $-0.527159$  a. u., which translates to an electron affinity of 0.739 eV. The measured electron affinity<sup>7</sup> for H is 0.754 eV.

The He basis is also the same as was used pre-

TABLE I. Slater-orbital basis sets.

H		Ne					
1s	1.60	1s	15.565 90				
	1.10		9.484 86				
	0.45		2s	7.792 42			
	2s		1.10	4.825 30			
			0.45	2.864 23			
	2p		1.20	1.961 84			
			0.85	1.31			
	3p		1.20	2p	9.134 64		
	3d		1.70	4.484 89			
	4d		1.70	2.381 68			
He							
1s	3.30			1.452 08			
	1.52			0.55			
2s	3.30	3d	3.82				
	1.52			1.31			
		4f	4.64				
2p	4.30						
	2.40						
				1.50			
3p	4.30						
				1.50			
3d	0.90						

viously<sup>6</sup> in SCF calculations, and yields a CI energy of  $-2.900\,305$  a. u., as compared to the spectroscopic value<sup>8</sup> of  $-2.9034$  a. u. The computed CI dipole polarizability for He is  $1.374a_0^3$ , which is very close to the accepted value<sup>9</sup> of  $1.383a_0^3$ .

The Ne basis was constructed from the  $(6s/4p)$  basis of Clementi and Roetti.<sup>10</sup> Diffuse  $2s$  and  $3d$  functions were added to the Ne basis, with exponents optimized for the maximum SCF dipole polarizability of Ne. The resulting basis was further augmented with tight  $3d$  and  $4f$  functions in order to describe the distortion of the atom at small internuclear separations. The computed SCF energy and dipole polarizability for Ne was  $-128.547\,055$  a. u. and  $2.364a_0^3$ . The accepted value<sup>9</sup> for the dipole polarizability of Ne is  $2.633a_0^3$ . Because of the type of CI calculation that we constructed for the NeH and NeH<sup>-</sup> systems, the SCF values are appropriate to the computations presented here.

For the molecular CI calculations, a SCF calculation was first performed on the  $X^2\Sigma$  neutral state and the  $X^1\Sigma$  ionic state to determine the respective spatial orbitals. In the HeH and HeH<sup>-</sup> calculations, all single and double excitations were allowed out of the occupied orbitals. Thus, the CI calculations include both inter and intra-electron correlation energy effects. The dimensions of the CI calculations were 1060 for HeH and 1054 for HeH<sup>-</sup>.

For the NeH and NeH<sup>-</sup> CI calculations, the  $1\sigma$  core orbital was kept fully occupied. The remain-

ing orbitals were divided into three sets; The inner shell, consisting of the  $2\sigma$ ,  $3\sigma$ , and  $1\pi$  orbitals, the  $4\sigma$  valence orbital, and the virtual orbitals. The CSF's of the CI calculations included single and double excitations from the inner and valence sets with respect to the configurations of the  $X^2\Sigma$  and  $X^1\Sigma$  states, with the restriction that no more than one electron is excited from the inner-shell orbitals. These calculations thus include the electronic correlation between the valence and inner shells, but exclude any electronic correlation for the inner shell which corresponds to the  $L$  shell of Ne. The dimensions of the CI calculations were 1988 for NeH and 2257 for NeH<sup>-</sup>.

### III. CALCULATIONAL RESULTS

The CI potential-energy curves for the  $X^2\Sigma$  state of HeH and the  $X^1\Sigma$  state of HeH<sup>-</sup> are presented in Table II and given graphically in Fig. 1. Since our calculations were not designed to yield an accurate description of the dispersion forces for the neutral state, it is not meaningful to compare our results in the van der Waals well region with those of Das *et al.*<sup>11</sup> However, on the repulsive wall it is appropriate to compare with the previous CI calculations of Miller and Schaefer.<sup>12</sup> At internuclear separations of 2.0, 3.0, and 4.0 $a_0$ , the values obtained by Miller and Schaefer and us, respectively, were 66.382 and 63.081 mH (milli-

TABLE II. Interaction potential energies for H, H<sup>-</sup> + He taken from the CI calculations,  $E(R)-E(\infty)$  in units of  $10^{-3}$  hartrees.

$R(a_0)$	$X^2\Sigma(\text{H} + \text{He})$	$X^1\Sigma(\text{H}^- + \text{He})$
1.5	131.546	181.610
1.8	84.718	132.687
2.0	63.081	107.455
2.2	46.762	86.555
2.4	34.468	69.305
2.6	25.240	55.221
2.7	21.540	49.226
2.8	18.349	43.859
3.0	13.238	34.785
3.5	5.664	19.532
4.0	2.271	11.113
5.0	0.032	3.796
6.0	-0.006	1.369
8.0	-0.016	0.169
10.0	-0.006	-0.004
15.0	-0.001	-0.013
20.0	-0.000	-0.004
25.0	-0.000	-0.002
30.0	-0.000	-0.001

Asymptotic total energies (hartrees)

$-3.400\,305$        $-3.425\,105$

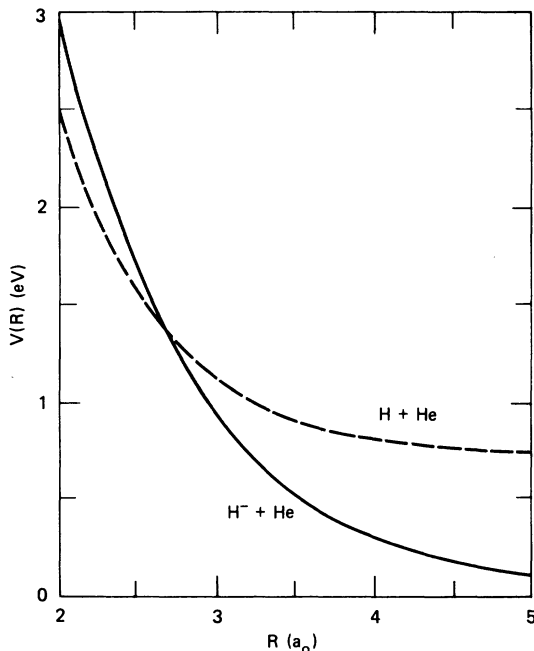


FIG. 1. Potential-energy curves for the  $X^1\Sigma$  state of  $\text{HeH}^-$  and the  $X^2\Sigma$  state of  $\text{HeH}$  calculated using the CI method.

hartree), 14.124 and 13.238 mH, and 2.484 and 2.271 mH. At all points the agreement is acceptable, with our values being slightly lower.

It is also instructive to compare the CI results to our previous SCF calculations.<sup>6</sup> At  $R = 3.0a_0$ , the values obtained from the SCF and CI calculations are 15.244 and 13.238 mH for  $\text{HeH}$  and 40.313 and 34.785 mH for  $\text{HeH}^-$ . Thus, we see the electron correlation included in the CI calculations has a larger effect on the negative-ion state than the neutral state for interactions low on the repulsive wall. Hence, when the neutral and negative-ion potential energies are compared to one another for the analysis of electron-detachment collision data, the SCF results will tend to overestimate the penetration of the negative-ion state into the continuum and the radius of the crossing.

The SCF and CI results for the ground states of  $\text{NeH}$  and  $\text{NeH}^-$  are given in Table III and the CI results are shown graphically in Fig. 2. Other CI calculations for  $\text{NeH}$  have been performed by Bondybey *et al.*<sup>13</sup> and Vasudevan,<sup>14</sup> but their results are presented graphically so no accurate comparison can be made. As for the  $\text{HeH}$  systems, we can see that the effects of including the electron correlation in the CI calculations has a larger effect on the negative-ion state than the neutral state when the comparison is made low on the repulsive potential wall.

Effects of quadruple excitations from the Har-

tree-Fock configuration were estimated by the formula due to Langhoff and Davidson.<sup>15</sup> Inclusion of quadruple excitations lowers the  $\text{H}^- + \text{He}$  asymptote by 0.11 eV and changed the  $\text{HeH}^-$  interaction potential by less than 0.04 eV for  $R \geq 3.0a_0$ . The effects of quadruple excitations on the  $\text{NeH}^-$  potential curve is even smaller. This is an artifact of our calculation which did not include any Ne intra-atomic double excitations.

#### IV. DISCUSSION

The motivating reason for performing these calculations was to try to shed some light on the mechanisms for threshold energy ( $E < 25$  eV) electron-detachment collisions. The  $\text{HeH}$  and  $\text{NeH}$  systems were chosen because the experimental cross-section data of Champion *et al.*<sup>16</sup> show very different behaviors. These data display reverse isotope effects with the  $\text{D}^- + \text{He}$  total electron-detachment cross section lying above that of  $\text{H}^- + \text{He}$  when plotted as a function of collision energy, while the  $\text{H}^- + \text{Ne}$  data are above those for  $\text{D}^- + \text{Ne}$ . Correspondingly, the elastic differential cross sections for  $\text{H}^- + \text{He}$  display a sharp threshold for electron detachment, while none is observed for  $\text{H}^- + \text{Ne}$ .

Probably one of the best ways to relate the calculated potential energies to the experimental data is to plot the difference in energies between the negative-ion and neutral states. In Fig. 3 we show the results of such plots for our SCF and CI calculations on the two systems studied. We should express caution at this point that neither the SCF or CI calculations were stabilized when the negative-ion state penetrated into the continuum, hence, the negative-ion curves can only be considered as qualitative in this region.

Apparent from Fig. 3 is the conclusion that both the SCF and CI calculations predict a sharp crossing into the continuum for the  $\text{HeH}$  system. The internuclear separation at this crossing is 2.70 and  $2.90a_0$  at energies of 1.34 and 1.23 eV for the CI and SCF calculations, respectively. A threshold energy of 1.34 eV is consistent with the experimental data,<sup>16</sup> along with the fact that one would expect to observe a distinct angular threshold for electron detachment on the differential cross sections for angles corresponding to turning points less than  $2.70a_0$ . Recent calculations by Gauyacq and Esaulov<sup>17</sup> place the crossing radius at  $2.1a_0$  with a threshold energy of  $\sim 2.6$  eV. Their calculations are in disagreement with our values.

The conclusion that the  $\text{HeH}^-$  penetrates deeply into the continuum and an electron-detachment model such as the complex potential method<sup>1</sup> is valid at threshold energies for this system is con-

TABLE III. Interaction potential energies for H,  $H^- + Ne$  taken from the SCF and CI calculations  $E(R) - E(\infty)$  in units of  $10^{-3}$  hartrees.

$R(a_0)$	$X^2\Sigma(H + Ne)$		$X^1\Sigma(H^- + Ne)$	
	SCF	CI	SCF	CI
1.5	240.058	223.410	245.722	242.659
1.75	172.408	151.648	190.074	176.603
2.0	124.955	104.314	154.750	132.254
2.25	88.204	70.720	123.415	97.918
2.5	60.919	47.347	95.282	71.558
3.0	27.842	20.553	53.370	37.274
4.0	5.217	3.261	15.666	9.835
6.0	0.140	-0.039	1.386	0.679
8.0	0.003	-0.023	0.052	-0.052
10.0	0.000	-0.006	-0.059	-0.085
15.0	0.000	-0.001	-0.023	-0.026
20.0	0.000	-0.000	-0.008	-0.009
25.0	0.000	-0.000	-0.005	-0.005
30.0	0.000	-0.000	-0.003	-0.004
Asymptotic total energies (hartrees)				
	-129.047 055	-129.047 055	-129.034 976	-129.074 214

firmed by the isotope dependence of the total electron-detachment cross sections. At a given collision energy, the complex potential model predicts the detachment probability is proportional to the amount of time the collision partners remain in the continuum or inversely proportional to the relative velocity. Thus, as shown by Lam *et al.*,<sup>1</sup> this theory confirms the larger cross section for

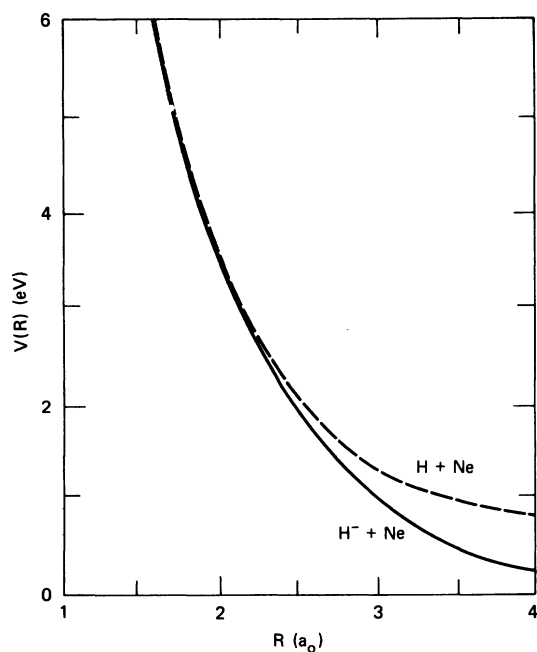


FIG. 2. Potential-energy curves for the  $X^1\Sigma$  state of  $NeH^-$  and the  $X^2\Sigma$  state of  $NeH$  calculated using the CI method.

$D^- + He$  as compared to  $H^- + He$ .

In a paper by Gauyacq,<sup>4</sup> the author applied a modification of Devdariani's model to  $H^- + He$  electron detachment from threshold energy to 25 eV.

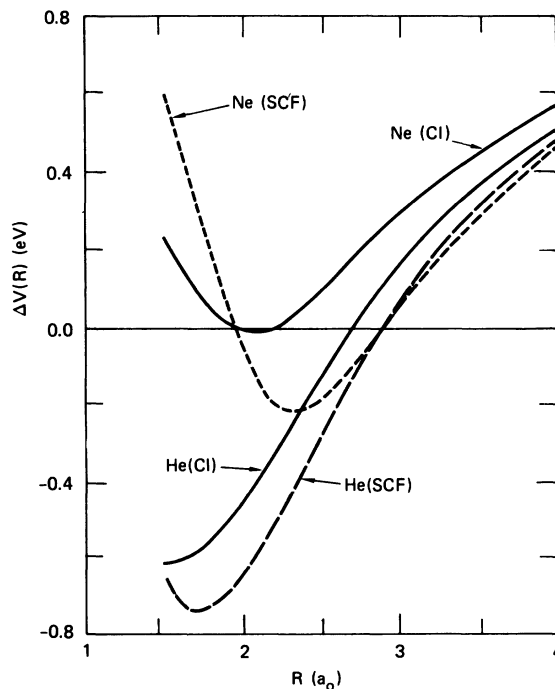


FIG. 3. Difference in potential energies between the neutral and negative-ion states of  $HeH$  and  $NeH$ . In order to obtain the correct asymptotic behavior, the negative-ion state has been shifted by 1.083 eV for the SCF calculations, 0.079 eV for the  $HeH$  CI calculations, and 0.015 eV for the  $NeH$  CI calculations.

Reasonable agreement with the experimental data was obtained. However, this agreement does not confirm the applicability of the model. In fact, examination of the formalism reveals that at collision energies of 10–25 eV, the cross section will be proportional to  $v^{2/5}$ . Therefore, the isotope dependence predicted by this model is in disagreement with the experimental observations.

Examination of Fig. 3 reveals that detachment in H<sup>-</sup> + Ne collisions will be very much different than that for H<sup>-</sup> + He. For NeH the negative-ion curve tends to merge with the continuum around  $R \approx 2.25a_0$  rather than cross sharply into it. Even the SCF calculations predict a very shallow penetration into the continuum. Hence, one would predict different cross-section behaviors for NeH than were observed for HeH. From the potential-energy curves, we would expect smaller cross sections for NeH than HeH at threshold energies, since the NeH negative-ion states do not penetrate deeply into the continuum to allow for strong coupling; such cross-section behavior is observed.<sup>16</sup> We would also not expect the complex potential method to be applicable to NeH. However, the method of Devdariani,<sup>5</sup> which is similar to a "charge transfer to the continuum" formalism, should lead to a reasonable comparison with experiment. Inherent in this model would be the prediction that the H<sup>-</sup> + Ne total detachment cross section will be larger than that for D<sup>-</sup> + Ne at the same collision energy, in agreement with experiment.

An interesting aspect of the potential-energy results is that the effective radius for electron detachment is greater for H<sup>-</sup> + He than for H<sup>-</sup> + Ne. If we use a rough estimate of the total electron-detachment cross section of  $\pi R_c^2$ , where  $R_c$  is the distance where the negative-ion and neutral state merge together, we would predict maximum cross sections of approximately  $\pi(2.7)^2 a_0^2 = 6.4 \times 10^{-16} \text{ cm}^2$  for H<sup>-</sup> + He and  $\pi(2.25)^2 a_0^2 = 4.5 \times 10^{-16} \text{ cm}^2$  for H<sup>-</sup> + Ne. Values close to these have been observed by Risley and Geballe<sup>18</sup> and Williams<sup>19</sup> and thus further substantiate our potential-energy calculations.

## V. CONCLUDING REMARKS

The potential-energy calculations on the neutral and negative-ion states of HeH and NeH indicate that the threshold-energy electron-detachment process ( $E < 25 \text{ eV}$ ) should be best described by the complex potential method for HeH<sup>-</sup> and a model such as that presented by Devdariani for NeH<sup>-</sup>. The merit of the latter model is that it does allow

for electron detachment at internuclear separations greater than where the neutral and negative-ion states merge together, and it does account for the breakdown of the Born-Oppenheimer approximation in this region. The accurate account of such behavior is especially important at higher collision energies.<sup>20</sup>

For the general case some combination of the above two models must be developed to describe the electron-detachment process. The complex potential method only allows transitions at separations where the negative-ion state is in the continuum. In contrast, the Devdariani model accounts for the transitions outside the merging point  $R_c$  of the two states and uses a  $(\text{const}) \times (\pi b_c^2)$  to describe the contribution to the total cross section for impact parameters  $b$  whose turning points are within  $R_c$ . Obviously, the true situation will require an accurate accord of the transitions induced in both regions.

*Note added in proof:* To further substantiate our prediction that the interaction potential followed by the H<sup>-</sup> + He collision partners does cross into the continuum, we have performed subsequent calculations on the HeH<sup>-</sup> and HeH systems. Additional diffuse hydrogenic orbitals of the type  $ns\sigma$ ,  $n\pi\sigma$ , and  $n\pi\tau$  ( $3 \leq n \leq 10$ ) were added to the H basis set given in Table I to represent continuum orbitals. A complete two-electron CI was then performed on HeH<sup>-</sup> and an SCF calculation on HeH (in this test we did not correlate the inner He(1s<sup>2</sup>) shell because doing a balanced calculation on both systems would require quadruple excitations for HeH<sup>-</sup>). In every test we found that the negative-ion curve crossed sharply into the continuum at  $\sim 2.7a_0$  with a threshold energy of  $\sim 1.4 \text{ eV}$ . At all  $R$  values, analysis of the orbitals showed H<sup>-</sup>(1s $n$ s) + He and H<sup>-</sup>(1s $n$ p) + He continuum states ( $3 \leq n \leq 10$ ) lying above the H + He neutral state. However, for  $1.5 \leq R \leq 2.5a_0$  a higher-lying eigenvalue was always found with a configuration close to that of H<sup>-</sup>(1s<sup>2</sup>) + He whose energy remained higher than that of the neutral state even under variation in the added hydrogenic orbitals. The penetration of the negative-ion state into the continuum is qualitatively reproduced by the numerical values given in Table II which did not include the continuum orbitals in the basis set.

## ACKNOWLEDGMENTS

This work was performed under a joint study contract between SRI and IBM. The work of one of the authors (R. E. O.) was supported by the MFE division of the U. S. Department of Energy.

- <sup>1</sup>S. K. Lam, J. B. Delos, R. L. Champion, and L. D. Doverspike, *Phys. Rev. A* **9**, 1828 (1974).
- <sup>2</sup>E. A. Mason and J. T. Vanderslice, *J. Chem. Phys.* **28**, 253 (1958).
- <sup>3</sup>E. A. Mason and J. T. Vanderslice, *J. Chem. Phys.* **28**, 1070 (1958).
- <sup>4</sup>J. P. Gauyacq, *J. Phys. B* **12**, L387 (1979).
- <sup>5</sup>A. Z. Devdariani, *Zh. Tekh. Fiz.* **43**, 399 (1973) [*Sov. Phys.-Tech. Phys.* **18**, 255 (1973)].
- <sup>6</sup>R. E. Olson and B. Liu, *Phys. Rev. A* **17**, 1568 (1978).
- <sup>7</sup>H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **4**, 539 (1975).
- <sup>8</sup>C. E. Moore, *Atomic Energy Levels* (U.S. G.P.O., Washington, D. C. 1949), Vol. I.
- <sup>9</sup>R. R. Teachout and R. T. Pack, *At. Data* **3**, 195 (1971).
- <sup>10</sup>E. Clementi and C. Roetti, *At. Data Nucl. Data Tables* **14**, 177 (1974).
- <sup>11</sup>G. Das, A. F. Wagner, and A. C. Wahl, *J. Chem. Phys.* **68**, 4917 (1978).
- <sup>12</sup>W. H. Miller and H. F. Schaefer III, *J. Chem. Phys.* **53**, 1421 (1970).
- <sup>13</sup>V. Bondybey, P. K. Pearson, and H. F. Schaefer III, *J. Chem. Phys.* **57**, 1123 (1972).
- <sup>14</sup>K. Vasudevan, *Mol. Phys.* **30**, 437 (1975).
- <sup>15</sup>S. R. Langhoff and E. R. Davidson, *Intern. J. Quantum Chem.* **8**, 61 (1974).
- <sup>16</sup>R. L. Champion, L. D. Doverspike, and S. K. Lam, *Phys. Rev. A* **13**, 617 (1976).
- <sup>17</sup>J. P. Gauyacq and V. Esaulov, *Electronic and Atomic Collisions*, edited by N. Oda and K. Takayanagi (North-Holland, Amsterdam, 1980), pp. 655-663.
- <sup>18</sup>J. S. Risley and R. Geballe, *Phys. Rev. A* **9**, 2485 (1974).
- <sup>19</sup>J. F. Williams, *Phys. Rev.* **154**, 9 (1967).
- <sup>20</sup>A. Herzenberg and P. Ojha, *Phys. Rev. A* **20**, 1905 (1979).