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Molecular states of HeH^+. Energies and dynamical couplings

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We complete the molecular results reported in a previous paper by presenting additional energies (for $^{1,3}\Sigma$ states) and radial couplings (between $^{1}\Sigma$ states) of the HeH^+ system. These results are needed to treat elastic and inelastic charge-exchange processes when full account is taken of momentum-transfer problems. We also present a formalism to calculate radial couplings between wave functions computed with the use of different variational methods and basis sets. The detailed form of the radial couplings is discussed and related to the Barat-Lichten correlation diagram. The effect of using finite basis sets in calculating degenerate molecular energies is also discussed.

I. INTRODUCTION

In a previous paper,[1] to be referred to as I, we have studied the simplest heteronuclear two-electron system, $He^+ + H$, and more specifically the reactions

$$^{4}He^{+}(1s)+H(1s)\rightarrow{}^{4}He^{+}(1s)+H(2p)\ , \qquad (1)$$

$$^{4}H^{+}(1s)+H(1s)\rightarrow{}^{4}He(1s\,2p)+H^{+}\ , \qquad (2)$$

with a six-term molecular expansion, using a semiclassical approach with linear trajectories at impact energies from 0.5 to 30 keV. The cross sections calculated with the use of this expansion agree quite well with experimental data, when the center of mass is chosen as the origin of electronic coordinates.

Another conclusion of paper I is that calculated cross sections for reactions (1) and (2) are strongly origin dependent for impact energies greater than 10 keV. This origin dependence can be directly traced and explained—using a simple model—to the origin dependence of the radial couplings. Our main conclusion was that translation factors must be included if the problem is to be solved correctly.

In this paper we present the energies and couplings between the molecular states which, in principle, should be considered in such a more complete treatment with translation factors and the form of these couplings is discussed in detail; in particular some of the couplings were not included in paper I because they did not vanish as $R\rightarrow\infty$.

It should be pointed out that the introduction of translation factors is not trivial, because the adequate form of the factor to be used at short distances is not known at present. Furthermore, in a recent study,[2] different known methods[3–5] to introduce these factors have been analyzed in detail for the case of approximate wave functions. The first conclusion of Ref. 2 is that the common translation factor (CTF),[5] unlike the other methods, maintains the convergence properties of the usual molecular expansion. A second important conclusion is that the methods of Bates and McCarroll[3] and that of projection over atomic components are prohibitively slow (by two orders of magnitude as compared to the standard method) when approximate wave functions are used. Fortunately, this is not the case for the CTF method. However, using different forms of the CTF at short and intermediate internuclear distances, one can obtain[2] widely different results for a truncated expansion. As a consequence, the origin dependence of the radial couplings in the standard molecular method may appear as a dependence on the specific form of the translation factor at short distances. It is, therefore, of the utmost interest to know the origin and the characteristics of the couplings between the standard molecular states, because to a good extent, the molecular calculation is independent of the particular form chosen for the TF.

Another important point is that when there are accidental near degeneracies as $R\rightarrow\infty$, the order in which the energy levels are obtained in a calculation is basis dependent. We point out that when two molecular states interact via a Demkov coupling, their order of appearance is irrelevant, except for very low collision energies.

We also present a formalism[6,7] which permits the calculation of radial couplings between approximate wave functions computed using different variational methods and basis sets. We compare our molecular results, for the states and internuclear distances of interest in this work, with the few ones found in the literature.

All molecular states presented here, and which can be introduced in a standard molecular treatment, will be included in the collisional calculation; these results are presented in the following paper. In that paper we calculate total cross sections (1) and (2), and also for the process

$$^4\mathrm{He}(1s^2)+\mathrm{H}^+ \rightarrow {}^4\mathrm{He}^+(1s)+\mathrm{H}(1s)\ . \qquad (3)$$

We have specifically studied the origin dependence of the three reactions and the transition probability for reaction (3) at fixed ΘE. An interesting feature, at high impact energies, is that the calculated cross sections for reaction (3) can either compete with those of processes (1) and (2) or be negligible compared to them, depending on the origin of electronic coordinates. To our knowledge, this is the first example of the dramatic effect of the origin dependence of radial couplings in calculations using the standard molecular model. Atomic units will be used unless otherwise stated.

II. RESULTS AND DISCUSSION

In this section we present the energies and couplings that will be needed in a treatment of processes (1), (2), and (3) when using a molecular model that takes into account the effect of momentum transfer. The energies and couplings involving Π states were reported in paper I and will not be repeated here.

Qualitative diagrams for the singlet and triplet states are presented in Figs. 1(a), and 1(b). Energies and couplings for $R \leq 0.6$ a.u. [molecular orbital (MO) region] were calculated with the single-center Gaussian-type orbital (GTO) expansions presented in Table I. The state that correlates in the UA limit to $1s\,2p$ ($1^1\Sigma$) was calculated using block diagonalization techniques[8] (see paper I for details) following the Barat-Lichten rules. A full configuration-interaction (CI) calculation was performed to obtain the energy corresponding to the $0^1\Sigma$ state. This was done in order to calculate the value of $\langle 0^1\Sigma \mid \partial/\partial R \mid 1^1\Sigma \rangle$ at small distances; this coupling would be exactly zero if block-diagonalization techniques were used for the $0^1\Sigma$ state, too. At the same time, this procedure eliminates the very sharp peak obtained by Green *et al.*[9] (origin of electronic coordinates on He), which is due to an avoided crossing between the energy of the $1^1\Sigma$ state and that which correlates to UA $1s\,2s$. This avoided crossing appears when full CI techniques are used to calculate both states. For $R > 0.6$ a.u. we use a full CI approach with a two-center basis set (Table I), which was approximately optimized for all states of interest, simultaneously.

For the ground ($0^1\Sigma$) state our energy results are only 1% above the very precise calculations of Kolos and Peak[10] and Green *et al.*[11] For the first two excited singlet states reported by Green *et al.*[11] our results are even closer to theirs. We have found no theoretical data to compare our results for the fourth to seventh ($3^1\Sigma$ to $6^1\Sigma$) states. For the first five triplet states ($1^3\Sigma - 5^3\Sigma$) our results are also within 1% of those of Green *et al.*[12] These molecular energies are presented in Table II.

Radial couplings have been calculated exactly using the method proposed by Macías and Riera.[6,7] The couplings between singlet Σ states which are relevant for the study of processes (1), (2), and (3) are presented in Figs. 2 – 6.

The $0^1\Sigma$-$1^1\Sigma$ coupling, which is due to delocalization effects and, therefore, decreases exponentially as $R \rightarrow \infty$, is presented in Fig. 2 for several choices of the origin of electronic coordinates, because we are going to study the origin dependence of reaction (3).

Two very important characteristics of the origin dependence of this radial coupling, which are also present in the radial coupling between the first two Π states (see paper I), and which we have found to be common to many systems and states are as follows.

(a) The origin-dependent term of the radial coupling $\underline{c}_i^\dagger \underline{\Gamma}\, \underline{c}_j$ (see Ref. 6) takes a non-negligible value for $R = 0$, when the two wave functions are of different parity in the UA limit.

(b) $\underline{c}_i^\dagger \underline{\Gamma}\, \underline{c}_j$ presents a steep maximum at intermediate internuclear distances ($R \sim 2$ in Fig. 2), where a single-center expansion is not adequate and where arguments based on UA properties are not valid.[2]

It should be noticed that evaluation of the $\langle 0^1\Sigma \mid \partial/\partial R \mid 1^1\Sigma \rangle$ for small distances involves the analytical evaluation of a radial coupling between wave functions obtained using different variational methods and basis sets, and which, therefore, are not exactly orthogonal. This means that Eq. (7) of Ref. 6 cannot be used to evaluate the first term of

$$\left\langle 0^1\Sigma \left| \frac{\partial}{\partial R} \right| 1^1\Sigma \right\rangle = \underline{c}_0^\dagger\, \underline{S} \frac{d}{dR} \underline{c}_1 + \underline{c}_0^\dagger\, \underline{B}\, \underline{c}_1 \qquad (4)$$

since that equation requires that $\underline{c}_0$, $\underline{S}$, and $\underline{c}_1$ appear in the same secular equation [Eqs. (3) and (4)

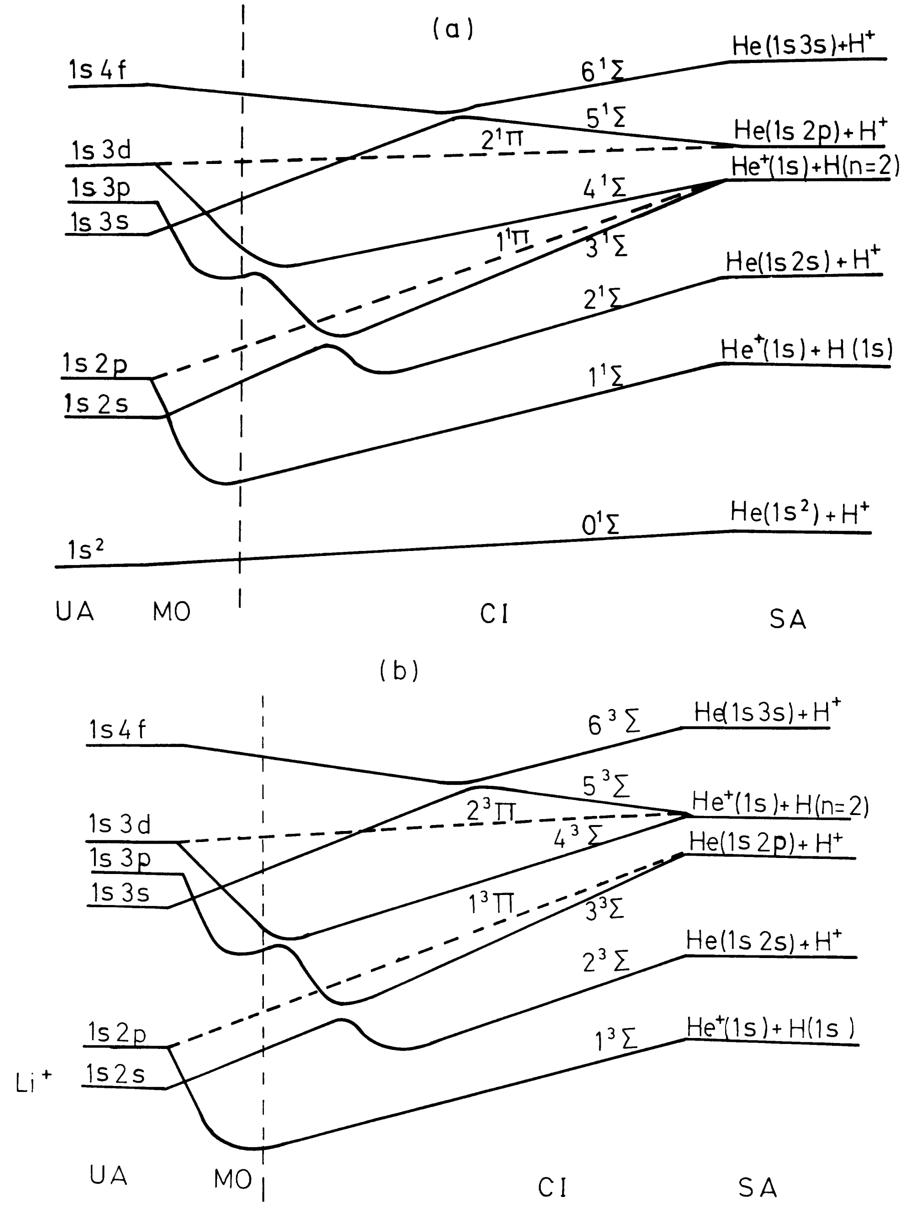

FIG. 1. Qualitative correlation for the (a) single and (b) triplet subsystems for reactions (1), (2), and (3) of text.

of Ref. 6].

We have solved this difficulty calculating explicitly $\underline{S}$ and $\underline{B}$ between the two basis sets and using[13]

$$\frac{d}{dR}\underline{c}_i=\underline{C}\,\underline{M}_i\underline{c}_i\,, \qquad (5)$$

where the ith row of $\underline{M}_i$ is $-\frac{1}{2}\underline{c}_i^{\dagger}(d/dR)\underline{S}$, and its jth row ($i\neq j$) is

$$\underline{c}_j^{\dagger}\left[\frac{d}{dR}\underline{H}-E_i\frac{d}{dR}\underline{S}\right](E_i-E_j)^{-1}\,. \qquad (6)$$

To our knowledge, this is the first calculation of this type. In the region of small internuclear distances the radial coupling obtained is practically antisymmetric; of course, it is exactly so for larger values of R where all calculated molecular states are orthogonal.

The $2^1\Sigma$-$3^1\Sigma$ coupling (see Fig. 3) presents a strong peak in the region of the corresponding avoided crossing, followed by a Demkov-type coupling. The avoided crossing can be predicted using the Barat-Lichten rules,[9] but the situation is some-

TABLE I. Exponents of the Gaussian orbitals used in the molecular calculation.

One-center expansion[a]			Two-center expansion[d]			
			He		H	
$\alpha 1s$, $\alpha 2p_z$ [b]	$\alpha 1s$	$\alpha 2p_z$ [c]	$\alpha 1s$	$\alpha 2p_z$	$\alpha 1s$	$\alpha 2p_z$
0.01	0.01	0.005	0.03	0.08	0.005	0.05
0.08	0.04	0.02	0.1	2.0	0.03	0.2
0.64	0.16	0.08	0.3		0.2	
5.00	0.64	0.32	1.0		1.5	
40.0	2.56	1.28	3.0		10.0	
	10.24	5.12	10.0			
	40.96	20.48				

[a] Origin: center of charge $R \leq 0.6$ a.u. [b] Used for the $0^1\Sigma$ state (full CI). [c] Used for all other $^1\Sigma$ and $^3\Sigma$ states (block diagonalization). [d] $R > 0.6$ a.u.

what more complicated than that described by Falcon *et al.*[14] As $R \rightarrow \infty$ the energies of states $2^1\Sigma$ and $5^1\Sigma$ are so close that the Stark interaction mixes them completely. One of the Stark combinations (at $R=\infty$) $(2s_{\mathrm{He}}+2p_{\mathrm{He}})$ is lower in energy than the Stark state $(2s_{\mathrm{H}}-2p_{\mathrm{H}})$ corresponding to state $3^1\Sigma$. At smaller distances delocalization effects result in charge distributions related to $3d$ $(2s_{\mathrm{He}}+2p_{\mathrm{He}})$ and $2s$ $(2s_{\mathrm{H}}-2p_{\mathrm{H}})$ orbitals. This effect is responsible for the maximum at $R \sim 15$ a.u. At smaller internuclear distances (4 a.u.) there will be an avoided crossing because the $2s$ orbital is lower in energy than the $3d$, in the UA limit (see also concluding remarks).

The 1-3 and 1-4 singlet Σ states present nonzero radial couplings as $R \rightarrow \infty$, which are identical and opposite in sign. In Fig. 4 this is not exactly so because the Stark components $(2s_{\mathrm{H}} \pm 2p_{\mathrm{H}})$ are not exactly degenerate in our calculation due to the fact that we are using a GTO expansion.

The $3^1\Sigma$-$4^1\Sigma$ coupling (see Fig. 5) presents a strong peak at $R \sim 3$ a.u. due to an avoided crossing which can be easily eliminated using block-diagonalization techniques. However, this would involve using a different method (block diagonalization for these two states) than for other states (CI), which we did not find convenient in the present work. The broad maximum at $R \sim 8$ a.u. is due to the Stark effect. It should be noticed that while Demkov-type radial couplings decrease exponentially with R, the Stark-type couplings decrease as R^{-3} (see Falcon *et al.*[14]).

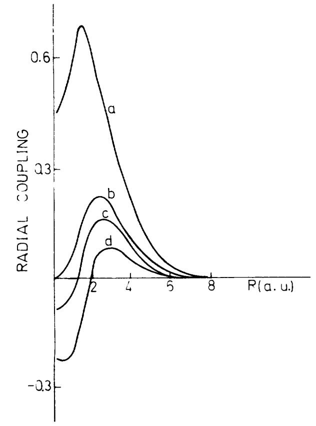

FIG. 2. Radial coupling between the $0^1\Sigma$ and the $1^1\Sigma$ states for different choices of the origin of electronic coordinates. (a) H$^+$; (b) center of charge; (c) center of mass; (d) ^{4}He^{2+}.

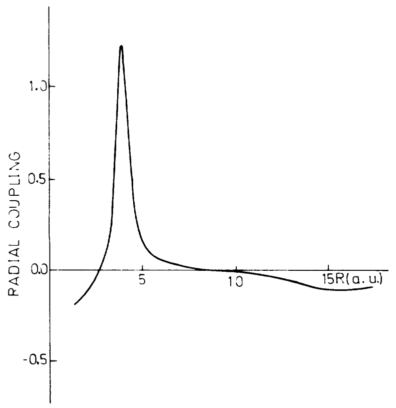

FIG. 3. Radial coupling between $2^1\Sigma$ and $3^1\Sigma$ states.

TABLE II. Molecular energies obtained using the basis sets of Table I for (a) singlet and (b) triplet states. We use the method of block diagonalization (see Ref. 8) for $R \leq 0.6$ a.u. and full CI for $R > 0.6$ a.u. Π state energies are those of paper I and are not included here.

(a)

R	$-E_0$	$-E_1$	$-E_2$	$-E_3$	$-E_4$	$-E_5$	$-E_6$
0.0	7.2442	4.9686	5.0300	4.7028	4.6923		
0.1	7.1005	4.8890	4.9351	4.6282	4.6123		
0.2	6.7932	4.7031	4.7320	4.4322	4.4253		
0.3	6.4415	4.4865	4.4996	4.2082	4.2067		
0.4	6.2000	4.3786	4.2692	3.9865	3.9908		
0.5	6.0927	4.2736	4.0521	3.7781	3.7885		
0.6	5.7643	4.0900	3.8815	3.6632	3.6701		
1.0	4.8559	3.5770	3.4501	3.2516	3.2201	3.2052	3.1287
1.5	4.2618	3.3262	3.0703	2.9321	2.8896	2.8518	2.7923
2.0	3.9080	3.2289	2.8572	2.7583	2.7189	2.6556	2.6084
3.0	3.5400	3.0868	2.6415	2.5842	2.5642	2.4644	2.4252
3.5	3.4393	3.0261	2.5800	2.5404	2.5191	2.4108	2.3728
4.0	3.3635	2.9675	2.5398	2.5072	2.4808	2.3708	2.3367
4.5	3.3063	2.9182	2.5165	2.4745	2.4490	2.3400	2.3132
5.0	3.2612	2.8761	2.5000	2.4445	2.4224	2.3154	2.2959
6.0	3.1940	2.8099	2.4698	2.3963	2.3796	2.2799	2.2723
7.0	3.1463	2.7617	2.4394	2.3605	2.3466	2.2670	2.2502
8.0	3.1095	2.7260	2.4094	2.3333	2.3207	2.2808	2.2298
10.0	3.0604	2.6752	2.3551	2.2905	2.2820	2.2574	2.2009
12.0	3.0270	2.6418	2.3101	2.2714	2.2549	2.2413	2.1796
14.0	3.0022	2.6179	2.2765	2.2536	2.2351	2.2223	2.1633
16.0	2.9843	2.6000	2.2537	2.2373	2.2198	2.2057	2.1510
18.0	2.9704	2.5861	2.2381	2.2225	2.2076	2.1921	2.1415
40.0	2.9093	2.5240	2.1767	2.1554	2.1517	2.1307	2.0872

The behavior of the $5^1\Sigma$-$6^1\Sigma$ coupling can be explained as follows. The state correlating in the UA limit to $1s\,3s$, according to Barat-Lichten rules (conservation of number of radial nodes) cannot be smoothly correlated with states involving $2s$ or $2p$ orbitals, on either He or H. It must correlate either to the He($1s\,3s$) or to a Stark mixture $[(1/\sqrt{3})3s_{\rm H}+(1/\sqrt{2})3p_{\rm H}+(1/\sqrt{6})3d_{\rm H}]$. Since the former state has a lower-energy limit as $R \rightarrow \infty$, the correlation is with that one. On the other hand, the UA $1s\,4f$ state correlates to $\mathrm{He}^{+}(1s)+\mathrm{H}$ ($n=2$) (see, however, the concluding remarks). The crossing between the $5^1\Sigma$ and $6^1\Sigma$ states occurs at $R \sim 6$ a.u. and, as we use a CI method in this region, it becomes an avoided crossing. A peak appears in the corresponding radial coupling (see Fig. 6).

Radial couplings between triplet Σ states are not discussed in detail because they do not present any new features. They are available from the authors upon request.

III. CONCLUDING REMARKS

It should be noticed that (in spite of the apparently complicated discussion presented in the previous section) the type and characteristics of the couplings can be predicted directly from the Barat-Lichten correlation diagram because the states involved in the UA limit constitute a Rydberg series. We give an illustration in Fig. 7. The $1s\,3p$ UA state [7(a)] can correlate smoothly to a Stark mixture He($1s\,2s+1s\,2p$) [7(d)] or to H($2s-2p$) [7(e)]. Energy considerations indicate that it correlates to 7(d). On the other hand, the $1s\,2s$ UA state [7(b)] can also correlate either to 7(d) or to 7(e). Again, energy considerations indicate that it correlates to 7(e). Then, there must be a Demkov-type radial coupling between states 7(a)−7(d) and 7(b)−7(e). For nonhydrogenlike systems the Stark mixture finally yields the spherical components 7(g) and 7(h). As the $1s\,3d$ UA [7(c)] correlates to the other Stark

TABLE II. (*Continued.*)

(b)

R	$-E_1$	$-E_2$	$-E_3$	$-E_4$	$-E_5$	$-E_6$
0.0	5.0052	5.1027	4.7427	4.7084		
0.1	4.9275	5.0070	4.6508	4.6289		
0.2	4.7470	4.8022	4.4545	4.4434		
0.3	4.5383	4.5679	4.2301	4.2268		
0.4	4.3700	4.3355	4.0079	4.0131		
0.5	4.2200	4.1166	3.7998	3.8134		
0.6	4.0886	3.9149	3.6065	3.6303		
1.0	3.7374	3.4682	3.2616	3.2264	3.1883	3.0951
1.5	3.5097	3.1100	2.9591	2.8768	2.8713	2.7309
2.0	3.3540	2.8882	2.7796	2.7183	2.6729	2.5589
3.0	3.1306	2.6718	2.6042	2.5688	2.4736	2.4436
3.5	3.0483	2.6170	2.5553	2.5215	2.4199	2.3771
4.0	2.9882	2.5863	2.5250	2.4849	2.3752	2.3425
5.0	2.8830	2.5369	2.4534	2.4204	2.3153	2.3089
6.0	2.8156	2.4986	2.4099	2.3729	2.2789	2.2703
7.0	2.7676	2.4620	2.3774	2.3376	2.2742	2.2576
8.0	2.7315	2.4279	2.3518	2.3099	2.2728	2.2480
10.0	2.6813	2.3703	2.3129	2.2721	2.2626	2.2066
12.0	2.6476	2.2387	2.2808	2.2521	2.2403	2.1926
14.0	2.6236	2.3005	2.2533	2.2339	2.2201	2.1844
16.0	2.6060	2.2816	2.2326	2.2171	2.2041	2.1663
18.0	2.5921	2.2673	2.2170	2.2082	2.1982	2.1530
40.0	2.5316	2.2060	2.1554	2.1525	2.1401	2.0837

component He$(1s\,2s-1s\,2p)$ [7(f)] there appear Stark-type radial couplings between states 7(a)–7(g) and 7(c)–7(h).

Smooth correlation indicates that the UA $1s\,3p$ state correlates to He$(1s\,2p)+\text{H}^+$ and the $1s\,4f$ correlates to He$^+(1s)+\text{H}$ $(n=2)$, yielding an avoided crossing between quasidegenerate states $4^1\Sigma$ and $5^1\Sigma$ which is not observed and is, therefore, not included in Fig. 1. Very often, calculated quasidegenerate states do not appear in the correct order, depending on the basis set used; it is, obviously, very important to know how this fact affects the results.

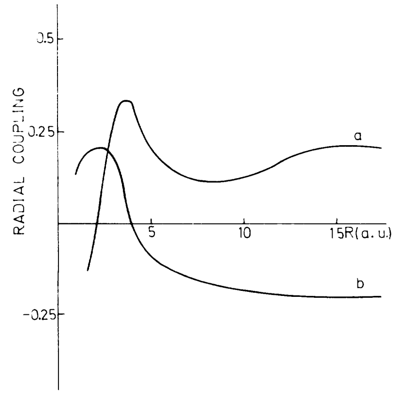

FIG. 4. Radial coupling between (a) $1^1\Sigma$ and $3^1\Sigma$ states, and between $1^1\Sigma$ and (b) $4^1\Sigma$ states.

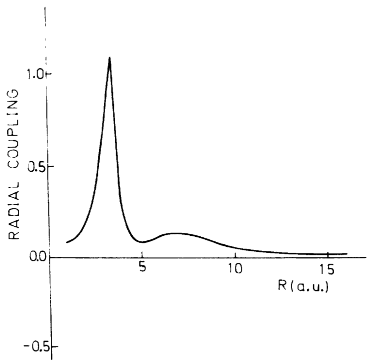

FIG. 5. Radial coupling between $3^1\Sigma$ and $4^1\Sigma$ states.

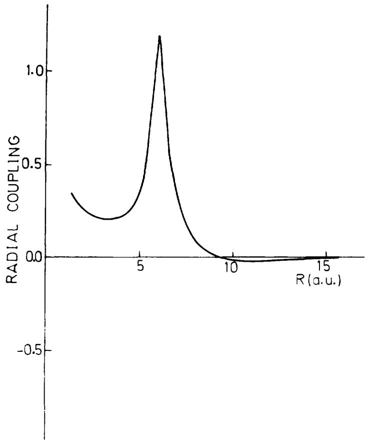

FIG. 6. Radial coupling between $5^1\Sigma$ and $6^1\Sigma$ states.

For example, in the case mentioned above, inverting the order of the $4^1\Sigma$ and $5^1\Sigma$ states eliminates the (unobserved) avoided crossing and the corresponding radial coupling. However, at high-impact energies the calculated transition probabilities and cross sections would be exactly the same whether the (quasidegenerate) states are in the correct order or not, as long as the couplings correspond to the particular set of states employed in the collisional calculation. Moreover, if the limit forms of Fig. 7 of two quasidegenerate states presenting a Demkov-type coupling are inverted the only change is the change of sign in the corresponding radial coupling.

This has a bearing on an argument which is often held on the use of dynamical couplings: Is it more important to use radial couplings which approximate the exact ones independently of the molecular energies, or should one use radial couplings calculated exactly between the approximate wave functions employed in the collisional treatment? In the case studied here, our conclusion clearly favors the second choice.

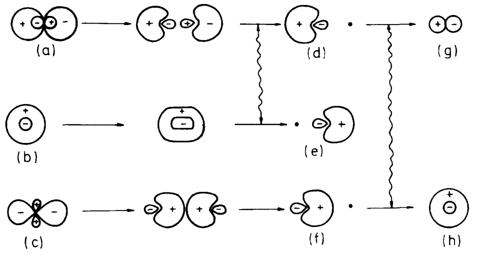

FIG. 7. Schematic shape of the orbitals φ as a function of internuclear distance for a Rydberg series $1s\varphi$, and following the Barat-Lichten rules. Steps as R increases correspond to (1) a passage from the UA limit to the MO region, (2) a delocalization process, and (3) (for nonhydrogenic systems) a passage from Stark hybrids to spherical orbitals. Radial couplings corresponding to delocalization and Stark effects are shown as wiggly lines. Limits (d), (e), and (f) follow from energy considerations. See text for details. He^{2+} is on the left in this figure.

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