

ence Foundation Grant No. DMR-81-06166 is gratefully acknowledged.

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¹P. W. Gibbs, C. G. Gray, J. L. Hunt, S. P. Reddy, R. H. Tipping, and K. S. Chang, *Phys. Rev. Lett.* **33**, 256 (1974).

²R. D. G. Prasad, M. J. Clouter, and S. P. Reddy, *Phys. Rev. A* **17**, 1690 (1978).

³W. Ivancic, T. K. Balasubramanian, J. R. Gaines, and K. Narahari Rao, *J. Chem. Phys.* **74**, 1508 (1981); T. K. Balasubramanian, Chen-Hsin Lien, J. R. Gaines, K. Narahari Rao, E. K. Damon, and R. J. Nordstrom, to be published.

⁴K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

⁵H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **38**, 176 (1960).

⁶M. Treffler, A. M. Cappel, and H. P. Gush, *Can.*

J. Phys. **47**, 2115 (1969).

⁷Chen-Hsin Lien, unpublished.

⁸G. Karl, J. D. Poll, and L. Wolniewicz, *Can. J. Phys.* **53**, 1781 (1975).

⁹J. D. Poll and R. H. Tipping, *Can. J. Phys.* **56**, 1165 (1978).

¹⁰If Γ is the EQQ coupling constant for the pair ($v = 0, J = 4$) and ($v = 0, J = 1$) and Γ' is the coupling constant for a pair in the $J = 1$ state, then the ratio of Γ to Γ' is equal to the ratio of the state average of the quadrupole moment over the appropriate initial and final states. Extrapolating the matrix elements of G. Karl and J. D. Poll [*J. Chem. Phys.* **46**, 2944 (1967)] to the $v = 0, J = 4$ state and using $\Gamma' = 0.54 \text{ cm}^{-1}$ given by S. A. Boggs and H. L. Welsh [*Can. J. Phys.* **51**, 1910 (1971)], we obtain $\Gamma = 0.55 \text{ cm}^{-1}$ in close agreement with the value of 0.559 cm^{-1} used in this analysis.

¹¹If we use $9E_{\text{QQ}}^2$ as an estimate of the second moment, assume a Gaussian lineshape, and compute E_{QQ}^2 for a pair of molecules in the $J = 1$ and $J = 5$ states, we obtain a FWHM of 9.6 cm^{-1} . The observed FWHM is 8.3 cm^{-1} .

¹²H. Stein, H. Stiller, and R. Stockmeyer, *J. Chem. Phys.* **57**, 1726 (1972).

Developments in the $\text{H}^+ - \text{H}^-$ Problem

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(Received 4 May 1981)

A one-electron treatment of the $\text{H}^+ - \text{H}^-$ collision is proposed which is not restricted to neutralization into $\text{H}(n=2) + \text{H}$, is free from two-state-crossing models, and involves an electron translation factor. Diabatic states are found to differ from those conventionally invoked. Neutralization into $\text{H}(n=3) + \text{H}$ is put forward and detachment is interpreted as a dynamic polarization effect. Agreement with available experiments is found above 200 eV (c.m.). Below this energy puzzling discrepancies persist.

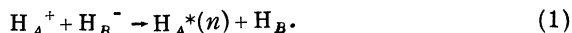
PACS numbers: 34.70.+e

The conventional treatment of the $\text{H}^+ + \text{H}^-$ mutual neutralization into $\text{H}^*(n) + \text{H}$ assumes transitions around crossings of the *Coulombic* ionic energy curve with *horizontal* covalent curves. Following Bates and Lewis¹ it has been agreed by some authors² that, according to the Landau-Zener (LZ) model,³ mutual neutralization at low energy ($E_{\text{c.m.}} < 20 \text{ eV}$) occurs predominantly into $\text{H}^*(n=3) + \text{H}$, whereas at moderate energies (50 eV $\lesssim E_{\text{c.m.}} \lesssim$ a few kiloelectronvolts) *neutralization into $\text{H}^*(n=2) + \text{H}$ prevails*. Most of the theoretic-

cal efforts to date have been devoted to the improvement of either the LZ curve-crossing parameters⁴ or the LZ model itself.⁵ Agreement with experiments was found accidentally when either incorrect LZ parameters or *ad hoc* adjustments were used.⁶ Dalgarno, Victor, and Blanchard⁷ were the first to abandon the simplistic LZ point of view and considered the $\text{H}^*(n=2 \text{ and } 3) + \text{H}$ channels within an *ab initio* close-coupling treatment. Unfortunately their calculations suffered from an inaccurate H^- binding energy

which prevented them from drawing definitive conclusions from that work. Subsequent close-coupling calculations⁸ never extended beyond $n=2$ channels and agreement with experiment could not satisfactorily be achieved. Moreover, some controversial claims concerning the effect of $n=3, 4$ channels have appeared recently (compare the relevant discussions in Refs. 1, 2, 4b, and 7 with that of Ref. 8b) but were not supported by detailed calculations.

In this Letter the $H^+ + H^-$ problem is revisited.⁹ We will be focusing herein on the salient features of our approach and main conclusions. An account of technical details is deferred to a future publication.¹⁰ To achieve an accurate representation of the relevant molecular properties of the system in the range of internuclear distances $5a_0 \lesssim R \lesssim 100a_0$, we modeled the problem in consideration of its essential characteristics. In either the incoming or the outgoing channels the system involves a *diffuse* electron moving in a *Coulomb potential* on one center (H^+) and a *short-range potential* on the other center (H). The second electron (in H) lying in a *compact* orbital is hardly expected¹¹ to contribute to the importance of the experimental neutralization cross section¹² which certainly results from transitions at relatively large R (the corresponding geometrical radius being $R_C \approx 19a_0$). With this assumption¹¹ the process we have been investigating is



Accordingly, the two-center one-electron Hamiltonian is

$$h = -\frac{1}{2}\Delta - 1/r_A + \mathcal{U}_B, \quad (2)$$

where \mathcal{U}_B representing the $e^- - H_B$ interaction has the form of a *nonlocal separable operator*^{13, 14}:

$$\mathcal{U}_B = -|g\rangle\lambda\langle g|, \quad (3a)$$

$$|g\rangle = (2\beta)^{1/2} |Y_0^0(\hat{r}_B)\exp(-\beta r_B)/r_B\rangle. \quad (3b)$$

The one-center Schrödinger equation for the model $e^- - H_B$ system involving \mathcal{U}_B lends itself to an exact analytic solution for both the bound and the continuous spectra. This property enables a straightforward determination of β and λ by fitting the single bound-state energy to the experimental H^- electron affinity and the singlet scattering s -phase shift to accurate theoretical results for $e^- - H$ elastic collisions.¹⁵

The adiabatic energy curves [eigenvalues of h in Eq. (2)] have been obtained in a basis set made of exact $\varphi_{nlm}(\vec{r}_A)$ hydrogenic wave functions (n

$\leq F$) and the exact solution $\chi(\vec{r}_B)$ of the model Hamiltonian for H_B^- . A polarization orbital $X_p(\vec{r}_B)$ was also considered in view of the high polarizability of H^- and in order to account for part of the transitions to the $e^- - H_B$ p continuum (the orbital X_p is derived from a perturbation treatment of the dipole interaction between the bound state χ of H^- and the corresponding free p -wave continuum). The calculated adiabatic energy curves compare quite satisfactorily with the available accurate *ab initio* results¹⁶ which lends support to the proposed model.

Turning to the collision problem, it has been known since the work of London¹⁷ and Zener^{3b} that processes of type (1) provide typical situations where the electron exchange can be handled by considering *diabatic* states. These states were thought to be merely the *valence bond* (VB) states that preserve the *pure* ionic and covalent characters. However, it was pointed out that such states entail nonorthogonality problems.¹⁸ In particular, in the region where the electron exchange takes place, the VB states have partially both ionic and covalent character. Consequently when building orthogonal states (as assumed in the definition of diabatic states)¹⁹ either (or both) the pure ionic or (and) covalent character should be lost or diluted. When looking for a representation of the VB type ensuring both diabaticity¹⁹ and orthogonality (as, e.g., a projected valence bond representation),²⁰ two possibilities readily suggest themselves: (i) preservation of the ionic character or (ii) preservation of the covalent character.

Representation (i) is generated by orthogonalization of the covalent states $\varphi_{nlm}(\vec{r}_A)$ to the ionic states $\chi(\vec{r}_B)$. The corresponding energy diagram and electronic couplings show¹⁰ an overall similarity with the *pure* ionic covalent scheme. However, this representation is *not diabatic* (if more than one covalent state is considered). Indeed, d/dR matrix elements generally exist between two covalent states. If center B is chosen as the electron coordinate origin spurious dynamic couplings $\langle nl m_A | \vec{v} \cdot \nabla_R | n' l_{\pm 1} m_A' \rangle$ show up at large R . If center A is chosen instead, this problem disappears but additional $d/dR|_A$ matrix elements couple the ionic and the modified covalent states.

In representation (ii) the ionic state $\chi(\vec{r}_B)$ is orthogonalized to all the considered covalent states $\varphi_{nlm}(\vec{r}_A)$. Choosing center A as the electron coordinate origin it can be shown that $d/dR|_A$ matrix elements appear *neither* between the modified ionic state and the covalent states *nor* be-

tween the covalent states themselves. This procedure generates the diabatic representation looked for, provided *the specific center A is taken as the electron coordinate origin* (see the discussion below on the electron translation factors). The corresponding potential energy diagram (Fig. 1) is rather unusual in the context of ionic-covalent interactions. Inspection of this diagram along with the off-diagonal terms of h shows (when $n \leq 3$) that the electron exchange process (1) pertains to *both* noncrossing (Demkov-Nikitin)²¹ and curve-crossing (LZ type) models.

Total cross sections for neutralization have been calculated in a basis extending up to $n = 3$ covalent states. All calculations²² were carried out within the impact-parameter method (IPM)²³ (test calculations involving a Coulomb trajectory²⁴ did not manifest significant differences in the considered energy range $E_{c.m.} \geq 30$ eV). Two types of calculations have been performed first. The first uses representation (i) with (the deliberate) complete neglect of dynamical couplings. The second uses representation (ii) with all its coupling (radial and rotational). As the two representations are equivalent when *all couplings* are considered, the comparison of the two calculations¹⁰ shows the dramatic role of dynamic transitions in representation (i) as well as that of transitions outside the curve crossings [*especially those towards $H_A^*(n=3) + H_B$*]. Although intrinsically instructive, these calculations do not agree with experiment.

Part of this failure is readily understood when we notice that, in the considered energy range $10 \text{ eV} < E_{c.m.} < 10 \text{ keV}$, the nuclear velocities

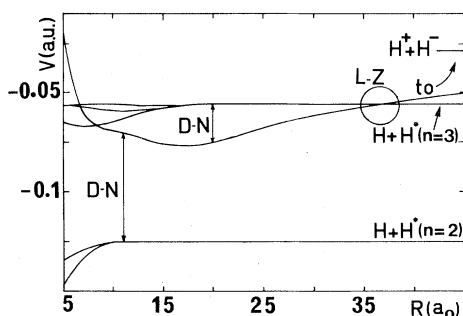


FIG. 1. $1\Sigma^+$ diabatic potential energy curves resulting from orthogonalization of the ionic state ($H^+ + H^-$) to the covalent states [$H^*(n \leq 3) + H$]. Transition regions between the modified ionic state and the covalent states are labeled L-Z and D-N in reference to Landau-Zener or Demkov-Nikitin-type models, respectively (Refs. 3 and 21).

might become of the same order of magnitude as those of the active loosely bound electron. The standard quasimolecular treatment is thus expected to break down unless electron translation factors (ETF) are taken into account.²⁵

We have selected to use ETF of the Schneiderman-Russek type²⁶ in a treatment where center B is moving with constant velocity with respect to the fixed center A . Accordingly, any orbital is multiplied by the common ETF $\exp(i\vec{f}\vec{v} \cdot \vec{r}_A)$ where the switching function is given by²⁷

$$f(\vec{r}, \vec{R}) = [R^3/(R^3 + b^3)] \left[\frac{1}{4}(e^{-aR})(2 + 3\eta - \eta^3) + (1 - e^{-aR})\theta(\eta) \right],$$

where $\eta = (r_A - r_B)/R$ and $\theta(\eta)$ is a step function that cuts off asymptotically terms behaving as R^{-1} arising from $1 - \eta$ in the derivatives of f . The parameters b ($=20a_0$) and a ($0.25a_0^{-1}$) were chosen to ensure the asymptotic conditions $f \rightarrow 1$ (or 0) around center B (or A) as $R > 40a_0$.¹⁰

All coupling terms²⁶ have been taken into account in an IPM treatment using representation (ii) with the above ETF incorporated. The basis set consisted of all states arising from $H_A^*(n=2 \text{ and } 3) + H_B$ along with $\chi(\vec{r}_B)$, the polarization function $X_p(\vec{r}_B)$, and its mate $\Pi_p(\vec{r}_B)$ under rotational coupling. The corresponding cross section for *mutual neutralization* reproduces the experimental data¹² from $E_{c.m.} \approx 200$ eV up to 10 keV, Fig. 2. In this energy range, the cross section de-

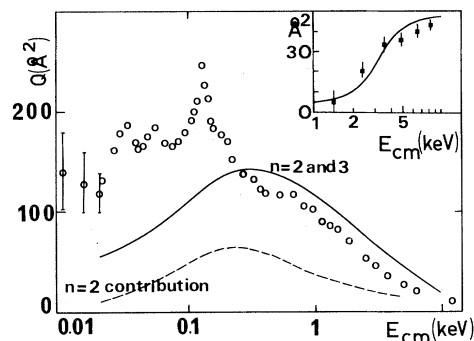


FIG. 2. Total cross sections for $H^+ + H^-$ mutual neutralization. Open circles, experimental data of Peart, Grey, and Dolder (Ref. 12b); the three data points on the left-hand side of the figure are from Moseley, Aberth, and Peterson (Ref. 12a). Full line, present theoretical result. Dashed line, contribution to the theoretical twelve-state cross section result of $H(n=2) + H$ channels. In the inset is shown the detachment cross section: full squares, measured by Hill, Geddes, and Gilbody (Ref. 29); full line, present calculation.

rived from the probability of populating X_p and Π_p (pseudostates in the H_B-e continuum) also nicely accounts for the experimental data on the detachment process²⁸ (see Fig. 2). This result entails an interpretation of this process as a dipole transition to the continuum under the effect of the polarization induced by the proton. Comparison of the theoretical cross sections of Fig. 2 with that of Ref. 8b shows the dramatic effects of the $n=3$ and detachment channels and the role of ETF.

Despite the above success the discrepancy seen in the neutralization cross section (Fig. 2) for $E_{c.m.} \approx 200$ eV is most disturbing. In view of the important contribution of the $n=3$ channels to the calculated cross section we have also investigated the effect of $n=4$ channels at $E_{c.m.} = 125$ eV.²⁹ It is found that these additional channels contribute negligibly to the already discussed results, in contradiction with the claim of Ref. 8b.

We conclude by stressing that the present work has attacked and consistently solved several problems which were disregarded or overlooked in previous investigations. Although they are the most elaborate to date our calculations still cannot fully account for the experimental data on mutual neutralization below $E_{c.m.} \approx 200$ eV.

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¹D. R. Bates and J. T. Lewis, Proc. Phys. Soc. London, Sect. A **68**, 173 (1955).

^{2a}R. E. Olson, J. R. Peterson, and J. T. Moseley, J. Chem. Phys. **53**, 3391 (1970).

^{2b}R. K. Janev and A. R. Tancic, J. Phys. B **5**, L250 (1972).

^{2c}R. K. Janev, Adv. At. Mol. Phys. **12**, 1 (1976).

^{2d}*The Physics of Ionized Gases*, Invited Lectures and Progress Reports of the Symposium on the Physics of Ionized Gases, edited by R. K. Janev (Institute of Physics, Beograd, Yugoslavia, 1978), p. 171.

^{2e}See also the discussion on the LZ model in A. Dalgarno, G. Victor, and P. Blanchard, Air Force Cambridge Research Laboratory Report No. 71-0342, 1971 (unpublished).

^{3a}L. D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932).

^{3b}C. Zener, Proc. Roy. Soc. London, Ser. A **137**, 696 (1932).

^{4a}R. Grice and D. R. Herschbach, Mol. Phys. **27**, 159 (1974).

^{4b}R. K. Janev, J. Chem. Phys. **64**, 1891 (1976).

⁵See Refs. 2b and 2d. See also A. A. Radtsig and B. M. Smirnov, in *Electronic and Atomic Collisions. Abstracts of Papers of the VIIIth International Conference, Amsterdam, 1971*, edited by L. M. Branscomb *et al.*

(North-Holland, Amsterdam, 1972), p. 481.

⁶As shown in Refs. 2c and 4, the LZ parameters of Ref. 2a (using the Smirnov formula) and of Ref. 2b were incorrect. As shown by B. Borondo, A. Macias, and A. Riera, Phys. Rev. Lett. **46**, 420 (1981), and by the present close-coupling calculations the result obtained in Ref. 2d, using a modified LZ model, is unrealistic.

⁷Dalgarno, Victor, and Blanchard, Ref. 2e.

^{8a}K. Roy and S. C. Mukberjee, Phys. Rev. A **7**, L130 (1970).

^{8b}Borondo, Macias, and Riera, Ref. 6.

⁹A preliminary account of the present work has been presented at the Huitième Colloque sur la Physique des Collisions Atomiques et Moléculaires (Abstracts of Papers), Louvain-la-Neuve, Belgium, 1980 (unpublished), and The Eleventh International Conference on the Physics of Electronic and Atomic Collisions (Abstracts of Papers), Gatlinburg, 1981 (unpublished).

¹⁰V. Sidis, C. Kubach, and D. Fussen, to be published.

¹¹Arguments supporting this claim are as follows: (i) the smallness of u-g splittings between the mate molecular states down to $R \approx 4a_0$ [see W. Kolos, J. Mol. Struct. **46**, 73 (1978)], (ii) the weak contribution of the H core-electron exchange, an upper bound of which can be estimated from $H^+ + H$ resonant charge exchange, and (iii) the recent results of Ref. 8b.

^{12a}J. T. Moseley, W. Aberth, and J. R. Peterson, Phys. Rev. Lett. **24**, 435 (1970).

^{12b}B. Peart, R. Grey, and K. T. Dolder, J. Phys. B **9**, L369 (1976).

¹³Y. Yamaguchi, Phys. Rev. **85**, 1628 (1954).

¹⁴Yu. N. Demkov and V. N. Ostrovskii, in *Zero Range Potential Method in Atomic Physics* (Leningrad Univ. Press, Leningrad, 1976); C. Botcher and V. Sidis, unpublished.

¹⁵C. Schwartz, Phys. Rev. **124**, 1468 (1961).

¹⁶See Kolos, Ref. 11. The present results deviate from those reported by Kolos and Wolniewicz at, e.g., $R = 8a_0$ and $12a_0$ by less than 2×10^{-3} and 5×10^{-4} a.u., respectively, for individual potential energy curves. Furthermore, the present adiabatic energy splitting in the $n=2$ "avoided crossing region" is reproduced to better than 5% which represents the accuracy of the computed adiabatic interaction in this region.

¹⁷F. London, Z. Phys. **74**, 143 (1932).

¹⁸R. Numrich and W. Truhlar, J. Phys. Chem. **79**, 2745 (1975).

¹⁹F. T. Smith, Phys. Rev. **179**, 111 (1969).

²⁰C. Kubach and V. Sidis, Phys. Rev. A **14**, 152 (1976).

²¹Yu. N. Demkov, Zh. Eksp. Teor. Fiz. **45**, 195 (1963) [Sov. Phys. JETP **18**, 138 (1964)]; E. E. Nikitin, in *Advances in Quantum Chemistry*, edited by Per-Olov Löwdin (Academic, New York, 1970), Vol. 5, p. 135.

²²These calculations involve impact parameters larger than $5a_0$ consistent with the proposed model. Although miscellaneous small R ($\approx 3a_0$) couplings are expected (curve crossings and rotational couplings) their effect is unlikely to alter our analysis as might be estimated from the corresponding geometrical cross section.

²³C. Gaussorgues, R. D. Piacentini, and A. Salin, *Comput. Phys. Commun.* 10, 223 (1975). This program has been modified for inclusion of additional matrix elements arising from the consideration of ETF (see text).

²⁴R. D. Piacentini and A. Salin, *Comput. Phys. Commun.* 12, 199 (1976).

²⁵See, e.g., W. R. Thorson and J. B. Delos, *Phys. Rev. A* 18, 117 (1978), for a recent review of this problem.

²⁶S. B. Schneiderman and A. Russek, *Phys. Rev.* 181, 311 (1969). Radial as well as rotational couplings

(proportional to v or v^2) have been considered in view of the closeness of the covalent energy levels and the fact that a traveling H^- orbital *does not have pure* Σ , Π , Δ symmetry.

²⁷K. Taulbjerg, J. Vaaben, and B. Fastrup, *Phys. Rev. A* 12, 2325 (1975).

²⁸B. Peart, R. Grey, and K. T. Dolder, *J. Phys. B* 9, 3047 (1976).

²⁹In view of the increasing bulk of the problem when including $n=4$ channels a test calculation has been performed with all σ states corresponding to $n=2, 3, 4$ along with χ and X_p .