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Unified quantum-defect-theory treatment of molecular ionization and dissociation

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Multichannel quantum-defect theory is extended to treat molecular dissociation processes simultaneously with ionization processes. Allowance is made for nuclear momentum coupling and for coupling with core excited channels. This theory combines the advantages of several less comprehensive approaches and is noniterative, nonperturbative, and applicable for arbitrary interaction strength. Several examples showing good agreement with experimental results relating to the H_2 molecule are given. [S1050-2947(97)51404-1]

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Ionization and dissociation ($I+D$) are the two fragmentation pathways available to a molecule. At high energy both are accessible and competition occurs between them. Reversal of one or the other leads to dissociative recombination (DR) or associative ionization (AI), reactions that play a key role in interstellar chemistry [1] or occur in cold collisions involving Rydberg atoms [2]. The interconversion of electronic and nuclear energy is mediated by bound states imbedded in the $I+D$ continua. This is ideally described by multichannel quantum-defect theory (MQDT), which treats discrete and continuum states in a unified fashion, extending scattering theory to negative energy [3]. We present an MQDT treatment for $I+D$ competition, which, unlike earlier treatments, is based entirely on clamped nuclei ion-electron scattering matrices and does not rely on a perturbation expansion. The treatment accounts for rovibronic coupling due to electronic core rearrangement and nuclear momentum coupling.

Since Fano's [4] first application of MQDT to a molecule, the range of molecular problems treated by MQDT has continued to expand. Building on Fano's pioneering work on rotational channel coupling, Jungen and Atabek [5] accounted for vibrational interaction and sketched out a nonperturbative treatment for electronic core rearrangement. We recently implemented these ideas in a full rovibronic MQDT treatment of the *gerade* levels of H_2, accounting for both singly and doubly excited electronic channels [6–9]. Meanwhile MQDT has been extended to treat rotational and vibrational autoionization simultaneously [10], and Giusti [11] has introduced a noniterative, perturbation-based, MQDT treatment of dissociative recombination. Giusti's approach was the first to calculate competition between preionization and predissociation [12] while accounting for electronic rearrangement in the core. In 1984 one of us introduced an iterative MQDT procedure that successfully studied $I+D$ competition, accounting for rotational and vibrational channel interaction [13]. Stephens and Greene [14] recently presented a simpler variant of the treatment of Ref. [13]. On a different track, Gao *et al.* [15] obtained very good agreement with experimental predissociation widths using a combined R-matrix MQDT approach.

Each of these previous treatments, however, has a limitation. The technique of Ref. [12] is applicable for weak interaction between Rydberg states and a dissociative valence state; that of Ref. [13] requires iteration and does not account for electronic core rearrangement; that of Ref. [14] is highly iterative and restricted to sharp, nonoverlapping, resonances; and that of Ref. [15] neglects electronic channel interactions and does not account for competition with preionization.

We combine the various strands to account for the full panoply of rovibronic interactions nonperturbatively and in the context of $I+D$ competition. Our procedure involves determining an effective reaction matrix K, which explicitly accounts for ionization and dissociation channels. Because this only needs to be done at a single energy in the region of interest our procedure is *noniterative*. Using the K matrix, physical boundary conditions can be imposed, allowing us to calculate $I+D$, their competition, DR, and AI, all without having to recalculate K. Electronic core rearrangement is accounted for and resonances of arbitrary width can be considered. We first present a concise description of our procedure, relying on reference to earlier work, and follow with a comparison of some initial results with experiment.

Already, in 1970, Fano [4] recognized the utility of the eigenchannel functions of the scattering problem. The physical wave functions can be expressed as linear combinations of the eigenchannel functions. The linear expansion coefficients are related to the elements of the diagonalizing transformation that can be determined as part of the solution of the eigenchannel problem.

For $I+D$, an eigenchannel function Ψ_β must have a common phase shift τ_β in all open channels in *both* the electron scattering direction $r\rightarrow\infty$ *and* in the dissociative direction $R\rightarrow\infty$. That is, Ψ_β must have the asymptotic form

$$\begin{aligned}\Psi_\beta(r\rightarrow\infty \text{ or } R\rightarrow\infty) &= \sum_{i\in P} T_{i\beta}[f_i(r)\cos(\pi\tau_\beta)-g_i(r)\sin(\pi\tau_\beta)]|i\rangle \\ &\quad+\sum_d T_{d\beta}[F_d(R)\cos(\pi\tau_\beta)-G_d(R)\sin(\pi\tau_\beta)]|d\rangle,\end{aligned} \tag{1}$$

where the sum on i is over all open ionization channels, and that on d is over open dissociation channels. There are as many independent functions Ψ_β as there are open channels.

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$f_i(r)$ and $g_i(r)$ are Coulomb functions describing the radial motion of the Rydberg electron, while $F_d(R)$ and $G_d(R)$ are numerically evaluated vibrational continuum functions chosen so that F_d is regular at $R=0$ and G_d is taken a quarter cycle out of phase. $|i\rangle$ represents the r-independent part of a rovibronic ionization channel, which is specified by the electronic i^+, vibrational v^+, and rotational N^+ state of the ion core, along with the l value of the Rydberg electron. $|d\rangle$ represents the R-independent part of a dissociative channel. Restricting our consideration to energies below the threshold for dissociative ionization, $|i:R\rightarrow\infty\rangle\rightarrow 0$ and $|d;r\rightarrow\infty\rangle\rightarrow 0$. Thus only one of the sums in Eq. (1) remains for a given limit. $T_{i\beta}$ and $T_{d\beta}$ are the elements of the matrix that diagonalizes the full $I+D$ scattering matrix. Inversion of this diagonalization leads to the effective $\overline{K}$ matrix for $I+D$,

$$\overline{K}_{mm'}=\tan(\pi\overline{\mu}_{mm'})=\sum_{\beta} T_{m\beta}\tan(\pi\tau_\beta)T^{\dagger}_{\beta m'}. \qquad (2)$$

The indices m and m' and the summation on β run over all open ionization channels $i\in P$ *and* all open dissociation channels d. $\overline{\mu}$, as defined in Eq. (2) is the quantum-defect matrix for $I+D$.

Imposing the boundary condition in the r direction given by the first summation in Eq. (1), Jungen and Dill [10] showed how to determine eigenchannel functions ψ_ρ appropriate for preionization with no dissociation. We divide the range of internuclear spacings R into an interior region $R\leqslant R_0$ and an exterior region $R\geqslant R_0$. The interior region is chosen as that in which configuration interaction is directly incorporated into the MQDT treatment (via off-diagonal elements of the electronic reaction matrix [7,8]). We then use the ψ_ρ of Ref. [10] in the interior region. The R-dependent factors of ψ_ρ are ion-core vibrational wave functions (including electronic adiabatic corrections) that vanish at a fixed large value of R, as appropriate when all dissociative channels are closed. The ψ_ρ therefore have different phase shifts in different dissociative channels and as such are not immediately appropriate for treating $I+D$. More clearly, the choice of vibrational functions that vanish at $R=R_0$ is equivalent to choosing a fixed logarithmic derivative (with respect to R), $-b=\infty$, at R_0. In dissociative scattering, however, the wave function at R_0 can have any logarithmic derivative. To account for dissociative scattering we therefore need a more general basis set in the interior region. We obtain this by performing several preionization calculations, determining a new set of ψ_ρ in each calculation. These preionization calculations differ in the choice of the logarithmic derivative imposed on the vibrational factors at R_0. Indexing these separate calculations by x, we denote the logarithmic derivative for set x by $-b^{(x)}$ and the resulting ψ_ρ eigenchannel functions by $\psi_\rho^{(x)}$. For each x we follow the procedure of Ref. [10] (which can be cast as a generalized eigenvalue problem [16]) and obtain the set of eigenchannel functions $\psi_\rho^{(x)}(R\leqslant R_0)$, their associated electronic eigenphases $\tau_\rho^{(x)}$, and the diagonalizing matrices $T_{i\rho}^{(x)}$, one for each of the open ionization channels. The $\psi_\rho^{(x)}$ are obtained in the sense that the linear coefficients $Z_i^{\rho(x)}$ of the rovibronic expansion

$$\psi_\rho^{(x)}(R\leqslant R_0)=\sum_i Z_i^{\rho(x)}\left\{f_i|i;(x)\rangle-\sum_j K_{ij}^{(x)}g_j|j;(x)\rangle\right\} \qquad (3)$$

are determined by imposing the boundary condition that $\psi_\rho^{(x)}(r\rightarrow\infty)$ takes the form of the first sum in Eq. (1), with $\tau_\rho^{(x)}$ taking the place of τ_β and $T_{i\rho}^{(x)}$ taking the place of $T_{i\beta}$. In Eq. (3) the sums on i and j are over all ionization channels (open and closed). K, the full vibronic reaction matrix [Eqs. (2)–(5) of Ref. [8]] is calculated from the R- and symmetry-dependent electronic body frame quantum-defect matrix. K involves integrals over the ionic vibrational wave functions and therefore depends on x.

A linear combination of all the resulting solutions, $\psi_\rho^{(x)}$, is sufficiently flexible to account for any logarithmic derivative at R_0 and therefore can be used to express the $I+D$ eigenchannel functions Ψ_β in the interior region

$$\Psi_\beta=\sum_{\rho,x} c_\rho^{\beta(x)}\psi_\rho^{(x)}(R\leqslant R_0). \qquad (4)$$

We thus require a procedure to determine the eigenphases of the full $I+D$ problem, τ_β, and the elements $T_{m\beta}=T_{i\beta}$ and $T_{d\beta}$ of the diagonalizing matrix of Eq. (1). As we shall see, this requires the determination of the linear coefficients $c_\rho^{\beta(x)}$ of Eq. (4). Once these quantities are determined the effective K matrix $\overline{K}$ of Eq. (2) can be calculated and used for $I+D$ and related processes.

To obtain these quantities we connect the interior expression of Eq. (4) to the exterior region $R\geqslant R_0$, and then impose the boundary condition of Eq. (1). We make the connection between the interior and exterior regions on each $\psi_\rho^{(x)}$. For a given x we have chosen the $\psi_\rho^{(x)}$ so that they all arrive at R_0 with the same logarithmic derivative $-b^{(x)}$. In the exterior region we neglect electronic configuration interaction and assume that in each dissociation channel d the system evolves adiabatically along a well-defined potential-energy curve. (Note that in the future a more complete treatment of interactions that occur at long range—such as the nonadiabatic avoided crossings between $H^+ + H^-$-ion pair states and covalent states—could be developed by incorporating a coupled-equations approach in the exterior region.) In the present approach the wave function in the exterior region can thus be written as a simple linear combination of functions for each dissociative channel. These functions are simply products of the same vibrational continuum functions F and G that we already met in Eq. (1), complemented by R-independent factors $|d\rangle$. Thus, in the exterior region, $\psi_\rho^{(x)}$ should take the form of the linear combination

$$\psi_\rho^{(x)}(R\geqslant R_0)=\sum_d T_{d\rho}^{(x)}[F_d(R)\cos(\pi\tau_d^{(x)}) - G_d(R)\sin(\pi\tau_d^{(x)})]|d\rangle. \qquad (5)$$

The vibrational continuum phase shifts $\tau_d^{(x)}$ must be such that at R_0 the logarithmic derivative (with respect to R) of the exterior function of Eq. (5) matches that of the interior function of Eq. (3), which is $-b^{(x)}$. The $\tau_d^{(x)}$ can thus be found by solving

$$-b^{(x)}=\frac{F_d'(R_0)\cos(\pi\tau_d^{(x)})-G_d'(R_0)\sin(\pi\tau_d^{(x)})}{F_d(R_0)\cos(\pi\tau_d^{(x)})-G_d(R_0)\sin(\pi\tau_d^{(x)})}. \tag{6}$$

Next, the linear coefficients $T_{d\rho}^{(x)}$ in Eq. (5) are obtained by projecting the interior function onto the exterior function. In the case in which there are no relevant dissociative channels differing only in the principal quantum number at the dissociative limit we obtain [13]

$$T_{d\rho}^{(x)}=\frac{\sum_{v^+N^+} Z^{\rho(x)}_{i=i^+lv^+N^+}\langle R_0|v^+\rangle\langle\Lambda|N^+\rangle}{\mathcal{N}_d(R_0)[F_d(R_0)\cos(\pi\tau_d^{(x)})-G_d(R_0)\sin(\pi\tau_d^{(x)})]}. \tag{7}$$

$\langle R_0|v^+\rangle$ is the value of the vibrational wave function at R_0. The rotational elements $\langle\Lambda|N^+\rangle$ of the frame transformation matrix are given in Eq. (14) of Ref. [8]. $\mathcal{N}_d(R_0)$ is the energy normalization factor at R_0 for the electronic state involved in channel d. Note that the rovibronic channel index i in Z_i includes v^+N^+, and that the sum over v^+N^+ and the vibrational and rotational factors must all be those appropriate for channel d and the imposed logarithmic derivative $-b^{(x)}$.

Choosing the entire set of $\psi_\rho^{(x=0)}$ functions as the initial basis, it is sufficient to complete this basis with one additional function $\psi_\rho^{(x\neq 0)}$ for each open dissociative channel in order that the expression for Ψ_β in Eq. (4) be sufficiently flexible to be able to find the same number of independent Ψ_β eigenchannel functions as there are open ionization and dissociation channels. We therefore choose one function from each set $\{\psi_\rho^{(x\neq 0)}\}$ and add it to the set $\{\psi_\rho^{(x=0)}\}$. We let q index the resulting set of pairs of ρ,x values that are actually included in Ψ_β in Eq. (4). We can therefore replace the indices ${}_\rho^{(x)}\leftrightarrow q$. Then $\tau_\rho^{(x)}\leftrightarrow\tau_q$ and $\tau_d^{(x)}\leftrightarrow\tau_d^q$ (τ_d^q depends on q solely through its dependence on x).

Imposing Eq. (1) as the boundary condition on Ψ_β in Eq. (4) leads to the generalized eigenvalue problem

$$S\vec{c}^{\beta}=\tan(\pi\tau_\beta)C\vec{c}^{\beta}, \tag{8}$$

where the matrices S and C have elements

$$C_{iq}=T_{iq}\cos(\pi\tau_q),\quad S_{iq}=T_{iq}\sin(\pi\tau_q),\quad i\in P;$$
$$C_{dq}=T_{dq}\cos(\pi\tau_d^q),\quad S_{dq}=T_{dq}\sin(\pi\tau_d^q), \tag{9}$$

and the coefficients c_q^β ($\equiv c_\rho^{\beta(x)}$) are arranged into the vector $\vec{c}^{\beta}$. Standard techniques give the full eigenphases τ_β and the coefficients c_q^β. The components of the full diagonalizing transformation are

$$T_{i\beta}=\sum_q c_q^\beta T_{iq}\cos[\pi(\tau_\beta-\tau_q)]\quad \text{for } i\in P,$$
$$T_{d\beta}=\sum_q c_q^\beta T_{dq}\cos[\pi(\tau_\beta-\tau_d^q)]. \tag{10}$$

This matrix is subjected to a symmetric orthogonalization procedure $T\rightarrow VT$, providing a criterion for optimizing the choice of imposed logarithmic derivatives $-b^{(x)}$ by permitting only small discrepancies of V from the unit matrix. The best results were obtained when the $-b^{(x)}$ were chosen so that for each set x an interior solution existed near the energy at which the calculation of K was being done. In the calculations presented below the mean absolute discrepancy was not greater than 0.001.

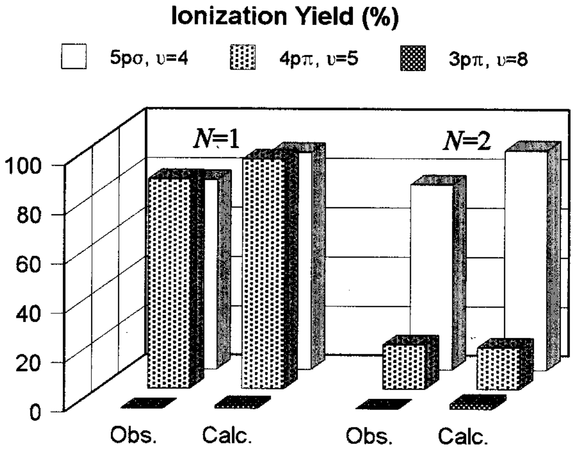

FIG. 1. Competition between ionization (shown) [17] and dissociation (100%-ionization) in excited levels of singlet *ungerade* H_2.

In practice a few ‘‘almost’’ open ionization channels are left open when calculating K, as in Ref. [13]. Thus these lowest closed channels are explicitly included in K, and do not introduce strong energy dependence characteristic of proximity to a resonance. This allows us to evaluate K at a single energy and then use it over a wide energy range. The ‘‘almost’’ open channels are closed in the last stage of the calculation, with the imposition of the physical boundary conditions.

We have shown how to determine the effective reaction matrix K, which contains the ionization and dissociation channels explicitly. Using K and imposing physical boundary conditions we can calculate $I+D$, their competition, DR, and AI. A separate calculation using this treatment must be performed for each total angular momentum N, space-fixed projection M, and total parity in which we are interested. We present two examples relating to H_2. The first concerns three *ungerade* $np\Lambda,v$ Rydberg resonances of H_2 lying closely together between the $v^+=1$ and 2 ionization thresholds of $H_2{}^+$. Each of these corresponds to $v-v^+>1$ and would be forbidden by the well-known propensity rule. Figure 1 compares our results with experiment [17] and shows that each level follows the pathway requiring the least interconversion of vibrational and electronic energy. Thus $3p\pi$, $v=8$ is fully predissociated, whereas $5p\sigma$, $v=4$ has a vibrational autoionization yield of about 80%. The remaining level $4p\pi$, $v=5$ corresponds to a delicate balance between the competing fragmentation pathways. Its behavior changes dramatically upon rotational excitation, decaying primarily into an ion and an electron for $N=1$, whereas for $N=2$ fragmentation into two neutral atoms prevails. Table I compares our results with observed resonance positions [18] and widths [19]. Our calculated yields and widths are of similar

TABLE I. Energies and widths (cm^{-1}) of singlet *ungerade* levels of H_2.

State		$N=1$ Energy	$N=1$ Width	$N=2$ Energy	$N=2$ Width
$5p\sigma,\ v=4$	obs.	127 599.4		127 666.9	
	calc.	127 602.2	0.38	127 669.7	0.48
$4p\pi,\ v=5$	obs.	127 667.6		127 758.7	
	calc.	127 665.4	0.046	127 758.4	0.024
$3p\pi,\ v=8$	obs.	127 248.2	3.4(3)	127 321.6	10.2(2)
	calc.	127 246.9	3.3	127 321.0	11.4

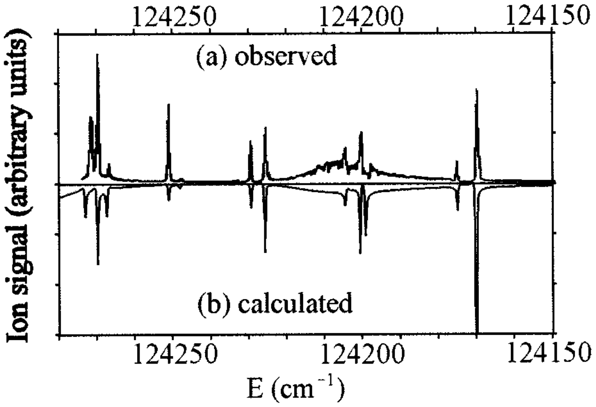

FIG. 2. Part of predissociation spectrum of singlet *gerade* H_2 excited from the $B\,^1\Sigma_u^+$, $v=0$, $N=0$ level. (a) Observed [21]; (b) calculated (present work).

quality to previous results [13,14], and the resonance positions are greatly improved. We stress that the only input data required are (i) the *ab initio* potential-energy curve of the ion along with its electronic adiabatic corrections, (ii) an energy-dependent quantum-defect function $\mu(R)$ for each of the $p\sigma$ and the $p\pi$ channels (obtained from *ab initio* potential-energy curves [20] by the Rydberg equation), and (iii) the electronic dipole transition moments for excitation from the H_2 ground state [10].

The second example concerns *gerade s* and *d* series built on the ion ground state. For these states strong predissociation is induced by electronic coupling with doubly excited channels built on the repulsive excited state of the ion. A full treatment of such states has not previously been available. Figure 2 shows part of the predissociation spectrum of Rottke and Welge [21]. Here sharp, slowly predissociating, Rydberg structures are superimposed on a broad, fast decaying resonance. Our calculation uses energy-dependent nondiagonal electronic quantum-defect matrices $\mu_{rs}^{\Lambda}(R)$ (obtained from *ab initio* potential-energy curves [20] and which account for core excitation as in Ref. [9]), and involves three dissociation channels $EF\,^1\Sigma_g^+$, $GK\,^1\Sigma_g^+$, and $I\,^1\Pi_g$. The dipole transition moments from the lower $B\,^1\Sigma_u^+$ state were calculated from the quantum defects in the same manner as in Ref. [22]. The expansion in Eq. (2) included 168 closed and 18 open rovibrational ionic channels. Although no ionization channel was open in this energy range the latter were included in the effective K matrix. These channels were closed by the imposition of the physical boundary conditions in the last step of the calculation and yielded the calculated resonances seen in Fig. 2.

In summary, the approach outlined here treats correlated motion of atoms and electrons in a diatomic molecule, while preserving the main advantage of quantum-defect theory: that the electronic wave functions are not explicitly required. The R-dependent quantum-defect matrices are the only dynamical parameters required and are directly related to the clamped nuclei potential-energy curves of the molecule. For energies below the threshold for dissociative ionization this procedure unifies the treatment of the different molecular fragmentation pathways into a single quantum-defect treatment based on the K matrix.

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