Vibrational Frame Transformation for Electron-Molecule Scattering

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The frame-transformation theory of electron interaction with a vibrating diatomic core is extended to allow for energy depedence of its parameters. The Born-Oppenheimer separation of electron and nuclear motion is preserved when the electron penetrates the molecular core. The extended theory reproduces the boomerang-model treatment of vibrational excitation in resonant e-N_2 collisions.

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A basic problem of molecular physics concerns the description of an electron incident on a vibrating molecule, charged or neutral.[1] Correlations between the electronic and nuclear degrees of freedom must be considered whenever an interconversion between electronic and vibrational energies can occur, as in vibrational excitation of molecules by electrons or vibrational autoionization. A natural theoretical starting point is to focus initially on the fixed-nuclei scattering phase shift $\pi\mu(\epsilon,R)$ characterizing the electron-molecular interaction in the body frame. This depends in general on the electron energy ϵ as well as on the nuclear separation R, and is defined by the asymptotic form of the fixed-nuclei electronic wave function,

$$\psi_R=\mathscr{A}\, r^{-1}\Phi_{\rm el}^{(N-1)}[f_\epsilon(r)\cos\pi\mu(\epsilon,R)-g_\epsilon(r)\sin\pi\mu(\epsilon,R)], \quad (1)$$

$r\geqslant r_0$. Here $\Phi_{\rm el}^{(N-1)}$ is the target electronic wave function (including also the spin and orbital wave functions of the Nth electron) and $f_\epsilon(r)$ and $g_\epsilon(r)$ are regular and irregular radial wave functions for the scattered electron with energy ϵ in the appropriate long-range potential. The symbol $\mathscr{A}$ implies antisymmetrization of the Nth electron with the target electrons. The boundary of the inner region or "reaction zone," beyond which exchange and correlation effects are unimportant, is denoted here by r_0.

Previous theoretical efforts to understand vibrational-excitation cross sections in electron-molecule collisions have been largely restricted to two opposite limiting extremes. The limit of resonant scattering is associated with a very strong energy dependence of $\pi\mu(\epsilon,R)$. When the incident electron can be trapped for several vibrations, the boomerang model of Herzenberg[2] defines a potential curve for the vibrational motion of the molecular complex. Its success in describing vibrational-excitation cross sections is well documented. Conversely, in the opposite limit of nonresonant scattering, the vibrational-frame-transformation theory of Chang and Fano[3] assumes that the nuclei are frozen when all electrons are in the reaction zone. Accordingly, a reaction matrix is constructed as a simple integral involving vibrational wave functions $\chi_v(R)$ of the target:

$$K_{vv'}=\int dR\, \chi_v(R)\tan[\pi\mu(R)]\chi_{v'}(R). \quad (2)$$

This extreme limit of energy-independent $\mu(R)$ (corresponding to a negligible electron time delay in the reaction zone compared to a vibrational period) is realized to a good approximation in the $np\lambda$ Rydberg states of H_2. Application of Eq. (2) has given very good agreement[4] with experimental energy levels and photoionization cross sections,[5] and recently[6] with photodissociation cross sections as well. [It should be pointed out that Eq. (2) emerges in only one limit of the Chang-Fano analysis. An equivalent expression had been previously derived in the context of nuclear scattering theory,[7] and its application to electron-molecule collisions is referred to as the "adiabatic-nuclei approximation" in Ref. 1.]

Recent work on electron-molecule scattering[8] has shown Eq. (2) to be inadequate when the energy dependence of $\mu(\epsilon,R)$ is significant. The adiabatic-nuclei approach works much better for e-H_2^+ than, e.g., for e-H_2 collisions, because the Coulomb acceleration gives even a low-energy electron a high speed within $r<r_0$ when the molecular core is charged. In practical terms, a problem arises because no obvious criterion exists for which ϵ to use in the matrix element (2), and because very different results can be obtained for different choices of ϵ. Consequently, the assumption that the nuclei are *frozen* when all electrons are in the reaction zone is no longer qualitatively correct. In response to this problem Schneider *et al.*[9] have developed an R-matrix formulation which can account for an arbitrary energy depen-

dence of $\mu(\epsilon,R)$, resonant or nonresonant. They expand the total wave function of the system inside the reaction zone in terms of a complete set of Born-Oppenheimer wave functions having a fixed (in practice, zero) logarithmic derivative on the reaction-zone boundary. *Several* potential curves are needed in order to achieve convergence of this expansion because the true scattering wave function does not obey a preselected boundary condition.

In this paper we identify a set of short-range wave functions ψ_α, each of which is a Born-Oppenheimer product corresponding to a *single* adiabatic potential curve. Moreover, this potential curve can be extracted directly from the fixed-nuclei scattering phase shift $\pi\mu(\epsilon,R)$, which is usually obtained in *ab initio* calculations. We thus obtain a frame-transformation theory in which the nuclei are not frozen while all electrons are inside the reaction zone.

Consider an electron in the field of an $(N-1)$-electron target molecule, having a potential energy curve $U^{(N-1)}(R)$ and vibrational wave functions $\chi_v(R)$ at energy levels E_v. Outside the target molecule, say at $r \geqslant r_0$, the Nth electron moves in a simple long-range potential, and each eigenchannel wave function ψ_α has the form[10,11]

$$\psi_\alpha = \mathscr{A}\, r^{-1} \textstyle\sum_v \{\Phi_{\mathrm{el}}^{(N-1)} \chi_v(R)\} U_{v\alpha} \times [f_v(r)\cos\pi\tau_\alpha - g_v(r)\sin\pi\tau_\alpha]. \qquad (3)$$

Equation (3) holds beyond roughly $r_0 \sim 10$ a.u. for nondipolar neutral targets. The target is described by vibrational wave functions $\chi_v(R)$ at energies E_v, and by an electronic wave function $\Phi_{\mathrm{el}}^{(N-1)}$. The regular and irregular functions (f_v, g_v) correspond to a channel energy $\epsilon_v = E - E_v$. The matrix $U_{v\alpha}$ in Eq. (3) consists of the eigenvectors of the reaction matrix $K_{vv'}$ and the $\tan\pi\tau_\alpha$ are its eigenvalues. When the long-range field is Coulombic, f_v and g_v can generally be taken to be energy-normalized Coulomb wave functions.[10,11] In electron-neutral scattering, instead, they are defined as "analytic" zero-field solutions for the appropriate partial wave l,

$$\begin{aligned} f_v^0(r) &= k_v^{-l}(2/\pi)^{1/2} r j_l(k_v r), \\ g_v^0(r) &= k_v^{l+1}(2/\pi)^{1/2} r n_l(k_v r). \end{aligned} \qquad (4)$$

Two things are essential in Eq. (3). Firstly, the summation over v may include closed channels with $\epsilon_v < 0$, in which case ψ_α is actually *divergent* at $r \to \infty$. On the other hand it is a *smooth* wave function at small distances, since the strong energy dependences (associated with resonances) arising from closed-channel elimination are not present. Secondly, in the case of electron-neutral scattering, the use of analytic solutions (f_v^0, g_v^0) removes complicated (e.g., Wigner) threshold effects from the reaction-matrix eigen-phase-shifts $\pi\tau_\alpha$ and eigenvectors $U_{v\alpha}$, which are then also analytic in E. Knowledge of the τ_α and $U_{v\alpha}$ yields an essentially exact wave function ψ_α at $r \geqslant r_0$ in closed form. Standard quantum-defect procedures[11,12] will then be applied to determine linear combinations of the ψ_α which are well behaved at $r \to \infty$ and energy normalized. The resulting eigenfunctions are characterized by a "physical" reaction matrix or scattering matrix, all of whose channels are open, correctly including threshold and resonance effects.

We proceed on the assumption that ψ_α is a Born-Oppenheimer product within $r < r_0$. The electronic factor must satisfy Eq. (1) on the reaction surface $r = r_0$, *and simultaneously* it must have the same eigen-phase-shift $\pi\tau$ in all channels v as required by Eq. (3). This will be achieved only if the fixed-nuclei phase shift is R independent, i.e., $\mu(\epsilon R) = \tau$ at all values of R. This requirement selects a body-frame energy $\epsilon^{(\tau)}(R)$ for each value of R, which adds to the target potential $U^{(N-1)}(R)$ to give the potential curve of the system,

$$U^{(\tau)}(R) = U^{(N-1)}(R) + \epsilon^{(\tau)}(R). \qquad (5)$$

The eigen-phase-shifts $\pi\tau_\alpha$ are finally identified by requiring that a vibrational energy eigenvalue coincide with the desired total energy E. We denote the normalized vibrational wave functions in this potential curve by $F_\alpha(R)$. When $(f_v, g_v) \sim (f_\epsilon, g_\epsilon)$ for all v at $r = r_0$, the eigenvectors of the smooth reaction matrix are simply Franck-Condon overlap integrals,

$$U_{v\alpha} = \int dR\, \chi_v(R) F_\alpha(R). \qquad (6)$$

(More accurate expressions can be derived if necessary.) The procedure just described amounts to an eigenchannel R-matrix calculation of the type outlined by Fano and Lee.[13] The energy is calculated as a function of the phase parameter τ, and the acceptable values of τ are those giving the correct energy E.

If $\mu(\epsilon,R)$ has no dependence on ϵ, the equation $\tau = \mu(\epsilon,R)$ has a solution at one R value (or a finite number) irrespective of ϵ. Hence $F_\alpha(R) \to \delta(R - R_\alpha)$ and the adiabatic-nuclei result of Eq. (2) is recovered. To show that our Born-Oppenheimer–based frame transformation can handle energy-dependent phase shifts $\mu(\epsilon,R)$ as well, we consider an application to resonant e-N_2 collisions in the $d\pi_g$ channel. Dubé and Herzenberg[14] have fitted experimental results with a Breit-Wigner profile in their boomerang calculation, obtaining $\epsilon_0(R)$ and $\Gamma(R)$ in the expression

$$\tan\pi\mu(\epsilon,R) = -\tfrac{1}{2}\Gamma(R)/[\epsilon - \epsilon_0(R)]. \qquad (7)$$

This phase shift $\pi\mu(\epsilon,R)$ is referred to the more usual energy-normalized zero-field solutions rather than to the analytic f^0 and g^0 of Eq. (4). The connection is given by $\tan\pi\mu^0(\epsilon,R) = [2\epsilon(R)]^{-l-1/2}\tan\pi\mu(\epsilon,R)$.

Because μ in Eq. (7) does not vanish at $\epsilon=0$, we assume instead a Breit-Wigner profile for the analytic $\mu^0(\epsilon,R)$ with the same $\epsilon_0(R)$ used by Dubé and Herzenberg, but with a rescaled width $\Gamma^0(R)=[2\epsilon_0(R)]^{-l-1/2}\Gamma(R)$ determined from their parameters. Figure 1 compares the resulting $\mu(\epsilon,R)$ and $\mu^0(\epsilon,R)$, showing how the latter is a much simpler and smoother function of both ϵ and R. This follows from the fact that the energy-normalized regular and irregular solutions of a free particle have a strong energy dependence at small r resulting from the centrifugal barrier. By defining the phase shift $\pi\mu^0$ with respect to solutions f^0 and g^0 which are energy independent at small r, we eliminate this trivial energy dependence from $\mu^0(\epsilon,R)$. The Born-Oppenheimer potential curve referring to motion within the reaction zone is then

$$U^{(\tau)}(R)=U^{(N-1)}(R)+\epsilon_0(R)-\tfrac{1}{2}\cot\pi\tau\Gamma^0(R). \qquad (8)$$

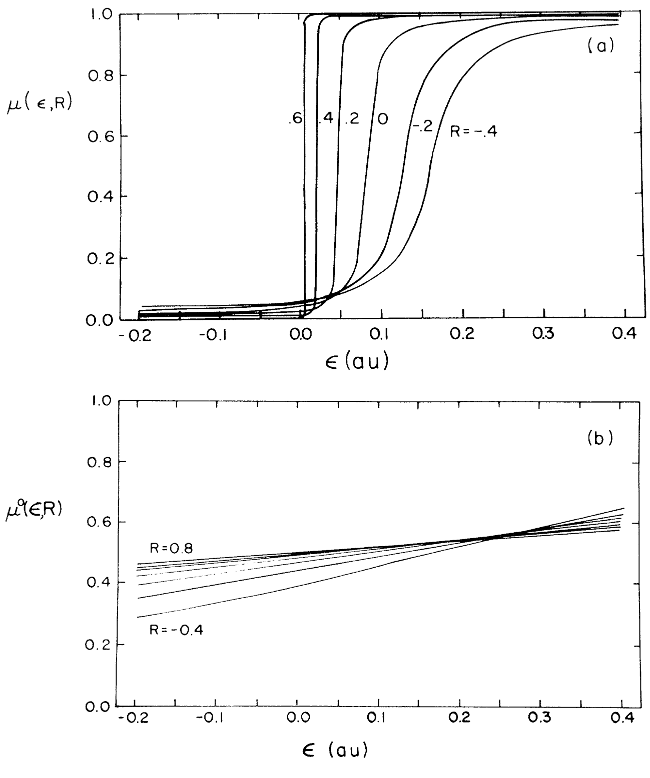

FIG. 1. The fixed-nuclei quantum defect for the $d\pi_g$ partial wave of an electron scattered by N_2 shown as a function of the body-frame energy ϵ and of the internuclear separation R measured from the equilibrium separation of N_2. The position and width of the Breit-Wigner profile is taken from Dubé and Herzenberg (Ref. 14). (a) Quantum defect $\mu(\epsilon,R)$ referred to energy-normalized zero-field solutions; (b) analytic quantum defect $\mu^0(\epsilon,R)$.

Since the dependence of $U^{(\tau)}(R)$ on τ is particularly simple for a Breit-Wigner profile, the allowed τ_α can be found by a simple variant of the iterative procedure outlined above. That is, the vibrational states $F_\alpha(R)$ in the potential $U^{(\tau)}(R)$ are expanded in states $\chi_v(R)$ of the target with coefficients $c_{v\alpha}$ to be determined. The equation determining the eigen-phase-shifts τ_α is then a standard generalized eigenvalue problem,

$$\sum_{v'}[(E_v-E)\delta_{vv'}+\langle v|\epsilon_0|v'\rangle]c_{v'\alpha}=\tfrac{1}{2}\Big(\sum_{v'}\langle v|\Gamma^0|v'\rangle c_{v'\alpha}\Big)\cot\pi\tau_\alpha. \qquad (9)$$

The eigenvectors $U_{v\alpha}$ coincide with $c_{v\alpha}$ in the approximation (6). The solution of (9) can be performed efficiently and on a coarse energy mesh since the $U_{v\alpha}$ and τ_α are insensitive to threshold effects and to most resonance effects. With a basis of twenty N_2 vibrational states the present calculation accurately converged.

Figure 2 compares several of our calculated cross sections for vibrational excitation of N_2 with experiment and with the semiclassical calculation of Dubé and Herzenberg. The good agreement demonstrates that this approach accurately describes resonant scattering processes in addition to the nonresonant and

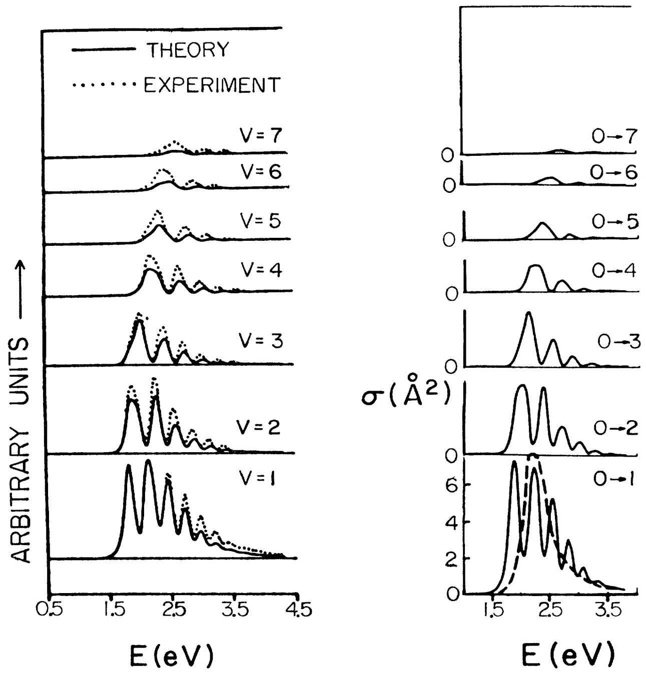

FIG. 2. Calculated cross sections for vibrational excitation of N_2 using the present formulation (right-hand side) compared with the experimental (Erhardt and Willman, Ref. 15) and theoretically fitted (Ref. 14) cross sections (left-hand side). Also indicated as a dashed curve on the right-hand side is the result for the 0→ 1 partial cross section which is predicted by Eq. (2).

near-threshold collisions handled by the adiabatic-nuclei theory. A few residual differences between the calculations are apparent in Figure 2, but their origin has not been determined. Note that we have *not* reoptimized any parameters from the Dubé-Herzenberg fit. The adiabatic-nuclei results are also shown in Fig. 2 for comparison, for the $0 \rightarrow 1$ partial cross section only.

To summarize, we have developed a unified treatment connecting energy-dependent fixed-nuclei scattering phase shifts to the full scattering matrix. When several partial waves interact at fixed R, the same procedure applies except that eigen-phase-shifts of a fixed-nuclei reaction matrix $K_{ll'}(\epsilon,R)$ are used in place of $\mu(\epsilon,R)$. In the present approach each eigenstate ψ_α is represented at small distances by a Born-Oppenheimer product associated with a single adiabatic curve and corresponding to a vibronic energy that coincides with the true energy E. In addition, each adiabatic curve $U^{(\tau)}(R)$ is related directly to the single-electron phase shift $\pi\mu(\epsilon,R)$. Dissociative channels could be readily incorporated into this approach along the lines described in Ref. 6.

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