Application of the non-adiabatic phase matrix method to vibrational excitation near a short-lived resonance: the case of e–H$_2$ scattering

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Abstract. We have applied the non-adiabatic phase matrix method for vibrational scattering processes to a system which supports an extremely broad (short-lived) shape resonance. This method provides a unified, systematic treatment of the range of physical effects that influence the collision as the nuclear geometry varies, from strongly resonant to purely background scattering. For this implementation we have chosen the prototypical $^2\Sigma_u$ shape resonance in e–H$_2$ scattering below 10 eV. We compare vibrational cross sections $0 \rightarrow 1$ and $0 \rightarrow 2$ from the present non-adiabatic theory to results from fully converged body-frame vibrational close-coupling calculations and from purely adiabatic studies using the energy modified approximation.

1. Introduction

The $^2\Sigma_u$ shape resonance in fixed-nuclei e–H$_2$ scattering has been the object of much attention throughout the development of theoretical methods for electron–molecule scattering calculations (Lane 1980, Domcke 1991). This resonance is responsible for an enhancement in the elastic and vibrational excitation cross sections which allows access to higher-lying states than can be populated appreciably by non-resonant scattering. This resonance also plays a key role in dissociative attachment. The strong interaction of this resonant state with the continuum of the system (neutral molecule plus free electron) for small internuclear separations makes it difficult to characterize the state in terms of a resonance energy and width (Nesbet 1981). Traditional methods based, for example, on fitting the eigenphase sum to a Breit–Wigner form, become ambiguous as the internuclear separation decreases.

Direct methods for computing a complex potential energy function for H$_2^-$ have been proposed using a variety of quantum chemistry techniques, such as the complex self-consistent-field method (McCurdy and Mowrey 1982), the projection-operator/configuration-interaction method (DeRose *et al* 1985), and the close-coupling bound-state approach (Gorczyca and Norcross 1990). Although not always in quantitative agreement with one another, results from such calculations clearly indicate that the resonance width decreases rapidly as the internuclear separation increases above equilibrium. The $^2\Sigma_u$ resonant state becomes bound at an internuclear separation around 2.8 a_0 (McCurdy and Mowrey 1982). Beyond this point, the potential energy curve for this state passes smoothly into the potential curve for dissociative attachment.

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This extreme variation in the resonance width over the experimentally relevant range of internuclear separations must be taken into account in theoretical calculations of vibrational excitation cross sections for e–H_2 scattering. This feature poses special problems for methods which treat the internuclear separation R *adiabatically*, as a parameter in the Born–Oppenheimer sense (Shugard and Hazi 1975); the most widely used such method is the adiabatic nuclear vibration approximation (Faisal and Temkin 1972). Elaborations of the adiabatic approach that are especially suited for near-threshold scattering include the first-order non-degenerate adiabatic method (Morrison 1986, Morrison *et al* 1979) and the energy-modified adiabatic approximation (Nesbet 1979). (For a review, see Morrison (1988).) The non-adiabatic phase matrix (NADP) method (Grimm-Bosbach *et al* 1996, Nesbet 1996) goes beyond these formulations in that it incorporates non-adiabatic effects within the context of the Born–Oppenheimer approximation (Schneider 1976) without resorting to CPU-intensive body-frame vibrational close-coupling calculations (Chandra and Temkin 1976, Morrison and Sun 1995). The NADP method also avoids the convergence limitation inherent in close-coupling methods which neglect continuum vibrational channels.

Nonadiabatic effects are most likely to be important at scattering energies near a relatively long-lived resonance (e.g. the $^2\Pi_g$ resonance at 2.9 eV in e–N_2 scattering). Here transfer of energy between kinetic energy of the projectile and vibrational degree(s) of freedom of the target occurs dynamically, an effect that might appear to preclude an approach based on fixed-nuclei scattering matrices. The NADP method, however, is just such an approach: an extension of the energy-modified adiabatic method (Nesbet 1979) that incorporates non-adiabatic effects and is based on fixed-nuclei R matrices. This method can be used both for vibrational excitation and dissociative processes (Nesbet 1996). To date the NADP method has been applied to resonant vibrational excitation in e–N_2 scattering (Thümmel *et al* 1995, Grimm-Bosbach *et al* 1996).

The extreme variation in the character of the Σ_u *S*-matrix, from strongly resonant at large R to clearly non-resonant at small R, poses a special challenge to adiabatic methods. This problem is illustrated by the fixed-nuclei Σ_u eigenphase sums in figure 1. At and below the equilibrium geometry, this eigenphase sum does not even pass through $\frac{1}{2}\pi$. By $R = 0.5\ a_0$, the smallest geometry that contributes to low-lying vibrational excitations of H_2, all trace of the shape resonance has vanished. Thus, the range of relevant internuclear separations encompasses quite different physical situations, from a pronounced shape resonance to purely background scattering. The challenge is to incorporate such diverse physics correctly and systematically in a formulation that preserves the highly desirable feature of working with fixed-nuclei quantities. In this paper we show that the NADP method accomplishes this goal.

An appealing feature of the NADP method is its foundation in R-matrix theory. (For an alternative approach to the inclusion of non-adiabatic effects in vibrational processes in e–H_2 collisions, see the applications of the Feshbach projection-operator method in Mündel *et al* (1985) and Berman *et al* (1985); for a review, see Domcke (1991).) The NADP method makes possible a consistent non-adiabatic treatment for all values of internuclear separations. The fixed-nuclei R-matrix, obtained from variational calculations at a set of internuclear separations R and fixed-nuclei continuum electron energies ϵ, is expressed in terms of a phase matrix $\Phi(\epsilon; R, r_0)$ that can be separated unambiguously into a foreground matrix $\Phi^1(\epsilon; R, r_0)$ and a residual background matrix $\Phi^0(\epsilon; R, r_0)$ at any R. The background phase matrix is converted to a vibronic phase matrix by the energy-modified adiabatic phase-matrix (EMAP) method (Thümmel *et al* 1995, 1992, Mazevet *et al* 1998)—an extension of the original energy-modified adiabatic approximation (Nesbet 1979) that is appropriate to weak variation with energy and internuclear separation. A matrix version of Breit–Wigner
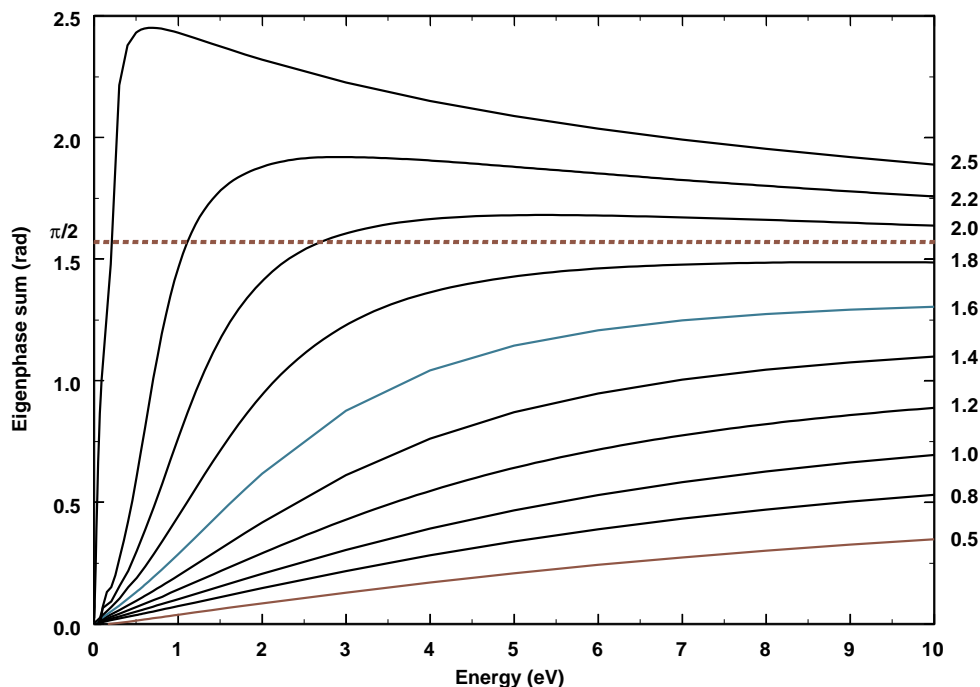
Figure 1. Eigenphase sums in the Σ_u symmetry for e–H$_2$ scattering at fixed internuclear separations (indicated on the right-hand axis in units of a_0). These were calculated from the *asymptotic K*-matrix, not the precursor phase matrix discussed in the text.

resonance analysis is used to convert $\Phi^1(\epsilon; R, r_0)$ to a vibronic representation (Nesbet 1996). The final *vibronic* phase matrix is the sum of the converted background and foreground phase matrices.

In the present implementation, we modify the NADP method as previously defined (Nesbet 1996) by defining a *dimensionless* phase matrix (section 2) and by removing the free-electron contribution (section 3). In section 4, we compare body-fixed Σ_u NADP cross sections for excitations from the ground state ($v = 0$) to the $v = 1$ and $v = 2$ excited states with results from the purely adiabatic EMAP method, and with benchmark results obtained using the body-frame vibrational close-coupling method (BFVCC). The benchmark status of the latter cross sections has been established by extensive comparison with crossed-beam data (Buckman *et al* 1990). For these low-lying vibrational excitation cross sections, the BFVCC method is a fully non-adiabatic treatment of the vibronic process in the limit of negligible contribution from the vibrational continuum. In contrast, the NADP method has the formal advantage of including, in principle, a complete representation basis for vibrational states (Nesbet and Grimm-Bosbach 1993), including the continuum, as does the projection-operator method. Both of the latter methods are therefore applicable to dissociative attachment. (For an alternative *R*-matrix-based formalism for the inclusion of non-adiabatic effects, see Schneider *et al* (1979a, b)).

2. The non-adiabatic phase matrix method

When the internuclear separation is fixed at a given value R, the coupled integro-differential equations for the radial part of the scattering electron wavefunction, written in the usual body-fixed reference frame with the z-axis coincident with the internuclear axis (Morrison 1988), are

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_b^2 \right] u_{\ell,\ell_0}^\Lambda(r; R) = 2 \sum_{\ell'} [V_{\ell,\ell'}^\Lambda(r; R) + \hat{\mathcal{V}}_{\ell,\ell'}^\Lambda(r; R)] u_{\ell',\ell_0}^\Lambda(r; R), \tag{1}$$

where the semicolon denotes the parametric status of R, the subscript ℓ_0 denotes the entrance channel, and $k_b^2/2 = \epsilon$ is the energy of the projectile in the body frame (in Hartree units). The quantum number ℓ corresponds to the electronic angular momentum of the scattering electron, and Λ to its projection along the internuclear axis. The coupling potential matrix elements are $V_{\ell,\ell'}^\Lambda(r; R)$ for the static plus (local) polarization potential and $\hat{\mathcal{V}}_{\ell,\ell'}^\Lambda(r; R)$ for the non-local exchange operator. In the remainder of this paper, we shall suppress the projection superscript Λ, it being understood that all quantities are referred to a particular value of this quantum number.

From the solutions of the integro-differential equations (1) fixed-nuclei R-matrices at a given R-matrix radius r_0 for a set of internuclear separations R and fixed-nuclei electron energies ϵ are defined by (Grimm-Bosbach *et al* 1996)

$$u_{\ell,\ell_0}(r_0; R) = \sum_{\ell'} R_{\ell\ell'}(\epsilon; R, r_0) \left[\frac{d}{dr} u_{\ell',\ell_0}(r; R) \right]_{r=r_0}. \tag{2}$$

The sum over ℓ' includes values consistent with the electron–molecule symmetry under consideration (e.g. for the Σ_u symmetry, $\ell' = 1, 3, \ldots$). In the NADP method, the fixed-nuclei R-matrix in (2) is replaced by a fixed-nuclei dimensionless phase matrix defined by the matrix relation

$$\tan \mathbf{\Phi}(\epsilon; R, r_0) = \mathbf{k}_b^{1/2} \mathbf{R}(\epsilon; R, r_0) \mathbf{k}_b^{1/2}, \tag{3}$$

where $\mathbf{k}_b$ is a diagonal matrix of (body frame) wavenumbers $k_b = \sqrt{2\epsilon}$. This definition differs from that given previously (Nesbet 1996) by the factors of $\mathbf{k}_b^{1/2}$, which render $\mathbf{\Phi}(\epsilon; R, r_0)$ dimensionless. Since this definition introduces branch-point behaviour at the continuum threshold, an appropriate analytic continuation is required for closed channels below threshold.

Fixed-nuclei resonances correspond to local maxima of the energy derivative of the eigenphase sum, i.e. of the sum of the arctangents of the (diagonal) elements of the diagonalized asymptotic K-matrix. By applying resonance analysis to the phase matrix in (3), which is defined at the R-matrix radius r_0, we can define the energy and width of a 'precursor resonance' at each R (Nesbet 1996). Each fixed-R precursor resonance can be associated with a physical scattering resonance (if one exists) when the R-matrix radius r_0 is extended to infinity, which introduces the effect of long-range potentials. Under the assumption that the background phase matrix varies linearly with energy, a precursor resonance energy $\epsilon_{res}(R, r_0)$ can be determined from the phase matrix of (3) as the value of the fixed-nuclei continuum energy ϵ at which

$$\left. \frac{d^2}{d\epsilon^2} \text{Tr} \, \mathbf{\Phi}(\epsilon; R, r_0) \right|_{\epsilon=\epsilon_{res}} = 0. \tag{4}$$

The 'precursor' status of $\epsilon_{res}(R, r_0)$ is signified by its parametric dependence on r_0. Applying Breit–Wigner resonance analysis to the fixed-nuclei phase matrix $\mathbf{\Phi}(\epsilon; R, r_0)$ at $\epsilon_{res}(R, r_0)$,

we can obtain the width $\gamma(R, r_0)$ of the precursor resonance from the eigenvalue equations (Smith 1960)

$$\left.\frac{\mathrm{d}}{\mathrm{d}\epsilon}\mathbf{\Phi}(\epsilon; R, r_0)\right|_{\epsilon=\epsilon_{\mathrm{res}}} \mathbf{y}(R, r_0) = \frac{2}{\gamma(R, r_0)}\mathbf{y}(R, r_0). \tag{5}$$

The elements of the eigenvectors $\mathbf{y}(R, r_0)$ are the projections of the resonant eigenchannels onto the original body-frame fixed-nuclei basis $\{|\ell; \Lambda\rangle\}$ (Nesbet 1980). It is important to note that, unlike a conventional Breit–Wigner analysis of the asymptotic eigenphase sum, this precursor resonance analysis can be applied at any internuclear separation, even at $R = 0.5\ a_0$, where no physical resonance exists (see figure 1).

Results of the precursor resonance analysis are used to construct the fixed-nuclei foreground phase matrix as a function of the fixed-nuclei continuum energy ϵ. This rapidly varying part is given by

$$\mathbf{\Phi}^1(\epsilon; R, r_0) = \mathbf{y}(R, r_0)\tan^{-1}\left[\frac{\gamma(R, r_0)}{2[\epsilon_{\mathrm{res}}(R, r_0) - \epsilon]}\right]\mathbf{y}^{\dagger}(R, r_0). \tag{6}$$

The slowly varying (background) phase matrix is then defined as

$$\mathbf{\Phi}^0(\epsilon; R, r_0) \equiv \mathbf{\Phi}(\epsilon; R, r_0) - \mathbf{\Phi}^1(\epsilon; R, r_0). \tag{7}$$

The *vibronic* phase matrix at r_0 can now be constructed as the sum of matrices calculated from the background and foreground fixed-nuclei phase matrices (6) and (7). The formal basis for this construction is replacement of the body-frame energy *parameter* ϵ by the *operator* $\hat{\epsilon} \equiv E - \hat{\mathcal{H}}^{(v)}$, where $\hat{\mathcal{H}}^{(v)}$ is the vibrational Hamiltonian of the neutral (Nesbet 1979). Formally, the (v, v') block of the vibronic phase matrix is

$$\mathbf{\Phi}_{v,v'} = \langle\phi_v|\mathbf{\Phi}^0(\hat{\epsilon}; R, r_0)|\phi_{v'}\rangle + \langle\phi_v|\mathbf{\Phi}^1(\hat{\epsilon}; R, r_0)|\phi_{v'}\rangle, \tag{8}$$

where $\phi_v(R)$ is the eigenfunction of the target Hamiltonian $\hat{\mathcal{H}}^{(v)}$ corresponding to eigenvalue E_v. Note that the operator $\hat{\epsilon}$ acts on functions of the vibrational coordinates.

To apply this formal result we must generate matrix representations of the functions in (8). The simplest of these is the background phase matrix. Because the background fixed-R phase matrix is slowly varying with R, we can treat this term using the (fully adiabatic) energy-modified adiabatic phase matrix (EMAP) method (Grimm-Bosbach *et al* 1996). In the diagonal elements we use fixed-R phase matrices evaluated at the eigenvalues $E - E_v$ of $\hat{\epsilon}$. In the off-diagonal elements we choose fixed-R phase matrices evaluated at a continuum energy equal to the geometric mean of the eigenvalues of $\hat{\epsilon}$ for the entrance and exit channels (Nesbet 1979),

$$\epsilon_{v,v'} \equiv [(E - E_v)(E - E_{v'})]^{1/2}. \tag{9}$$

Evaluation of the foreground vibrational phase matrix, the second term in equation (8), requires integrals over R of the fixed-nuclei quantity (6) with ϵ replaced by $\hat{\epsilon}$ in the denominator. We evaluate this integral by introducing a complete set of functions of R defined by the eigenvalue equation

$$[\hat{\mathcal{H}}^{(v)} + \epsilon_{\mathrm{res}}(R, r_0)]\chi_s(R) = E_s\chi_s(R). \tag{10}$$

(For clarity, we suppress the dependence of $\chi_s(R)$ and E_s on the R-matrix radius r_0.) Notice that in this equation, the precursor resonance energy $\epsilon_{\mathrm{res}}(R, r_0)$ plays the role of an additional 'electronic potential energy'. We solve equation (10) in a basis of spline-delta functions (Nesbet and Grimm-Bosbach 1993). The resulting eigenfunctions $\chi_s(R)$ diagonalize the energy denominator in (6) when ϵ is replaced by $\hat{\epsilon}$. We then construct the

vibronic foreground phase matrix *entirely in terms of fixed-R quantities*. The (v, v') block of this matrix is†

$$\Phi^1_{v,v'}(E) = \tan^{-1} \sum_s \langle \phi_v | \boldsymbol{y}(R, r_0) \gamma^{1/2}(R, r_0) | \chi_s \rangle$$
$$\times [2(E_s - E)]^{-1} \langle \chi_s | \gamma^{1/2}(R, r_0) \boldsymbol{y}^\dagger(R, r_0) | \phi_{v'} \rangle. \tag{11}$$

This is the key equation of the NADP method; introduction of the complete set $\{\chi_s(R)\}$ includes short-range (inner region) non-adiabatic effects at the R-matrix boundary r_0 within the context of a fixed-R (Born–Oppenheimer) treatment. Use of this equation requires only separation of the fixed-nuclei phase matrices at r_0 into slowly varying (background) and rapidly varying (foreground) parts; it therefore is valid even though the range of relevant internuclear separations include values where no physical resonance exists.

   Having constructed the vibronic background phase matrix using the EMAP method and the foreground matrix via equation (11), we simply add the two to obtain the vibronic phase matrix corresponding to total energy E,

$$\boldsymbol{\Phi}(E) = \boldsymbol{\Phi}^0(E) + \boldsymbol{\Phi}^1(E). \tag{12}$$

From this matrix, the corresponding vibronic R-matrix is obtained via

$$\boldsymbol{R}(E) = \boldsymbol{k}^{-1/2} \tan \boldsymbol{\Phi}(E) \boldsymbol{k}^{-1/2}, \tag{13}$$

where the elements of the diagonal matrix $\boldsymbol{k}^{-1/2}$ are

$$[\boldsymbol{k}^{-1/2}]_{v,v'} = k_v^{-1/2} \delta_{v,v'}. \tag{14}$$

This R-matrix is then propagated into the asymptotic region, where it is transformed into a vibronic K-matrix from which cross sections are calculated. In this 'outer region' $r > r_0$, non-adiabatic effects are fully taken into account via coupling of the eigenfunctions of $\hat{\mathcal{H}}^{(v)}$, as in the BFVCC formulation.

3. The free-electron phase matrix

In conventional scattering theory for a spherical interaction potential, phase shifts are defined relative to free waves via the usual asymptotic boundary conditions (Taylor 1972). In conventional electron–molecule scattering theory, where the interaction potential is non-spherical, the analogous quantity is the eigenphase sum, which is calculated from the asymptotic K-matrix (see Morrison (1988) and references therein). The phase matrix (3), however, contains a contribution due to free waves, which we call the free-electron phase matrix. As is evident from (2), the R-matrix for a free electron is diagonal; its elements are equal to the inverse logarithmic derivatives of spherical Bessel functions of order ℓ. The free-electron phase matrix is therefore diagonal; its matrix elements are proportional to the inverse tangent of the inverse logarithmic derivative of these functions,

$$\Phi^{\text{FE}}_{\ell,\ell'}(\epsilon; r_0) \equiv \tan^{-1} \left[\sqrt{2\epsilon} \frac{j_\ell(k_b r_0)}{j_{\ell'}(k_b r_0)} \right] \delta_{\ell\ell'}. \tag{15}$$

From the definition of the dimensionless phase matrix (3), it follows that the precursor phase sum, which can be calculated from the fixed-nuclei phase matrix $\boldsymbol{\Phi}(\epsilon; R, r_0)$, includes a contribution from the free-electron matrix (15).

   To facilitate precursor resonance analysis for small internuclear separations, we subtract the contribution of the free-electron phase matrix from the fixed-nuclei phase matrix

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† The separation of $\gamma(R, r_0)$ into the product $\gamma^{1/2}(R, r_0)\gamma^{1/2}(R, r_0)$ is essential for the extension of this method to dissociative attachment and is discussed in Nesbet (1996).

$\Phi(\epsilon; R, r_0)$. That is, in practice, we perform the resonance analysis described in section 2 on a modified phase matrix defined by

$$\tilde{\Phi}(\epsilon; R, r_0) \equiv \Phi(\epsilon; R, r_0) - \Phi^{\text{FE}}(\epsilon; r_0). \tag{16}$$

Because the free-electron phase matrix $\Phi^{\text{FE}}(\epsilon; r_0)$ is independent of the internuclear separation R, it contributes only to diagonal elements of the full vibronic phase matrix (12). The separate components of the vibronic phase matrix combine additively to give, for the (v, v') submatrix,

$$\Phi_{v,v'}(E) = \tilde{\Phi}^0_{v,v'}(E) + \tilde{\Phi}^1_{v,v'}(E) + \Phi^{\text{FE}}(E; r_0)\delta_{v,v'}, \tag{17}$$

where we note that determination of the last term via the EMAP prescription for the continuum energy $\epsilon = \epsilon_{v,v'}$ of (9) results in a free-electron phase matrix that corresponds to total system energy E.

4. Results

We have applied the NADP method to fixed-nuclei e–H$_2$ R-matrices obtained by solving the integro-differential equations (1). In these and the comparison calculations reported here, the electron–molecule interaction potential consists (Trail *et al* 1990) of a static term based on a near-Hartree–Fock target electronic wavefunction, an exchange term that rigorously incorporates this non-local interaction (Trail 1991), and a parameter-free polarization potential which approximates short-range bound–free correlation and dynamic distortion effects (Gibson and Morrison 1984). For each fixed-nuclei electron energy ϵ and internuclear separation R, the corresponding R-matrix is constructed using (2) at a radius $r_0 = 10\ a_0$. For e–H$_2$, this value of r_0 ensures that only the asymptotic part of the polarization potential remains outside the R-matrix sphere and that non-local exchange effects are negligible in the outer region, $r > r_0$.

In figure 2 we present the precursor potential energy curve. This function is defined at each internuclear separation as the sum of the precursor resonance energy $\epsilon_{\text{res}}(R, r_0)$ and a Morse potential, which we use to represent the electronic energy of the neutral H$_2$ target; this function is therefore the total electronic potential energy in equation (10) for the expansion basis $\{\chi_s(R)\}$.

It is important to appreciate that the function in figure 2 differs from the 'resonance energy curve' as usually defined, i.e. the real part of the complex potential-energy function for nuclear motion in the transient negative-ion state (Nesbet 1991), because it neglects long-range potentials outside the R-matrix radius r_0. The usual resonance energy curve for e–H$_2$ collisions, which has been studied previously (McCurdy and Mowrey 1982, DeRose *et al* 1985, Gorczyca and Norcross 1990), shows a bound H$_2^-$ state at $R \approx 2.8\ a_0$, reveals a well-defined resonance state for slightly smaller values of R, and merges smoothly into the background for $R \lesssim 1.7\ a_0$. In contrast, the precursor potential energy curve in figure 2, which is distinct from the neutral electronic energy curve at all R and depends on r_0, is a mathematical construct whose definition is linked through the function $\epsilon_{\text{res}}(R, r_0)$ to the R-matrix boundary r_0. It is important to note that the precursor resonance potential energy does account for coupling between nuclear and electronic motion inside the R-matrix sphere via the complete set of states $\{\chi_s(R)\}$ used to calculated the foreground vibronic phase matrix $\Phi^1(E)$.

Moreover, unlike the usual resonance energy curves, the precursor resonance potential in figure 2 is well defined at all internuclear separations. This feature facilitates the calculation

(a)

(b)
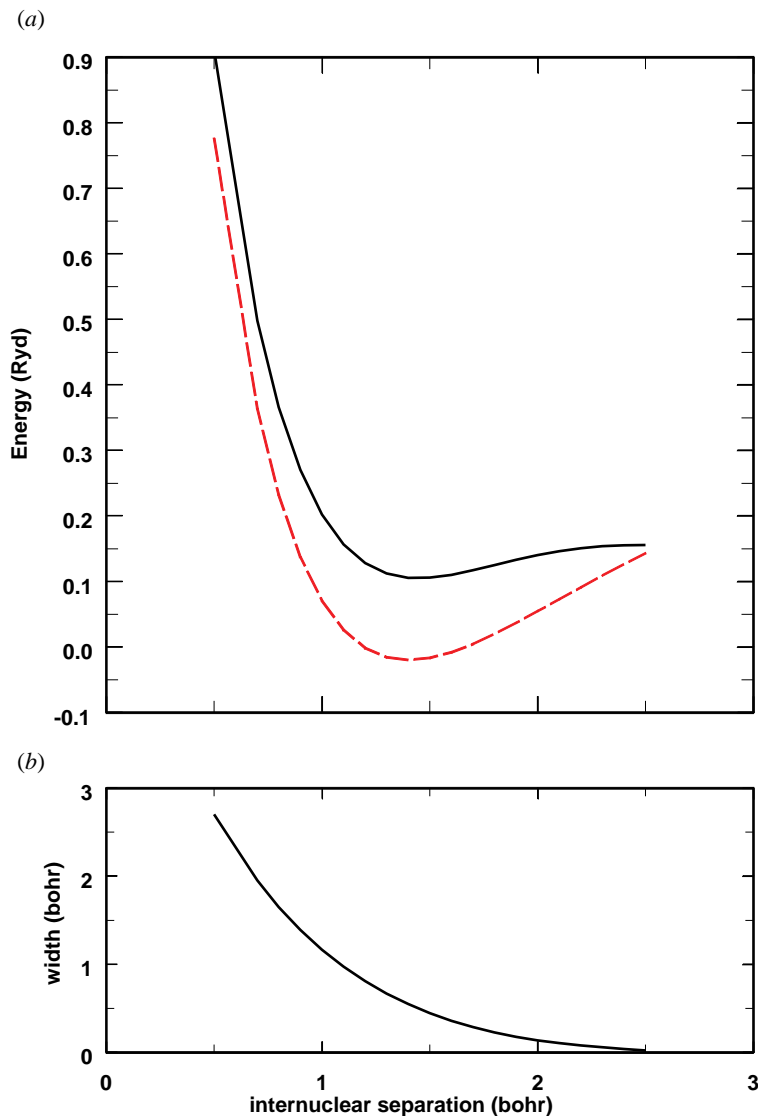
Figure 2. (a) The effective potential energy for the precursor resonance (full curve): the sum of $\epsilon_{\mathrm{res}}(R, r_0)$ and the ground electronic state potential energy of H_2 (broken curve). (b) Variation of the precursor resonance width function $\gamma(R)$ with internuclear separation.

of cross sections—especially at small values of R, where, as seen in figure 1, the fixed-nuclei resonance shades into the background. At such values of R, the decomposition (17) simply becomes irrelevant and the resulting vibronic R-matrix equals that generated by the *adiabatic* EMAP method, which pertains to situations where non-adiabatic effects have negligible influence.

The consequences of this smooth merging of non-adiabatic and adiabatic physics, an important characteristic of the NADP method, is evident in figure 3, which shows the Σ_{u} partial cross sections for $0 \rightarrow 1$ and $0 \rightarrow 2$ vibrational excitation. For both excitations, the NADP and EMAP results are quite similar, and both agree with the fully non-adiabatic
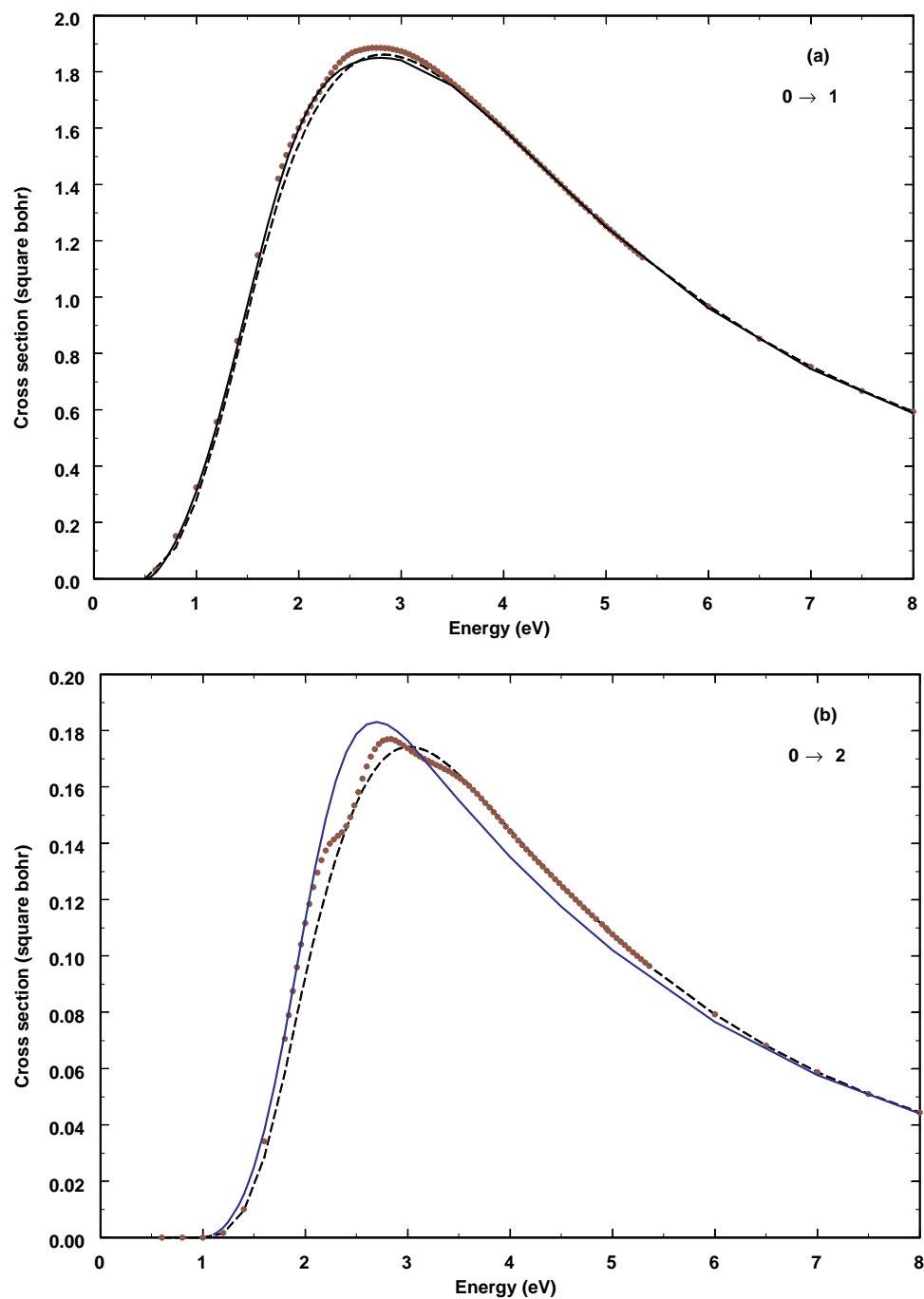
Figure 3. The $^2\Sigma_u$ partial cross section for excitation of H$_2$ from the ground vibrational state to the (*a*) $v = 1$ and (*b*) $v = 2$ states, as calculated using (——) the BFVCC, (- - - -) the EMAP method and (●) the NADP method.

BFVCC results to within the roughly 1% numerical accuracy of these calculations. (In the EMAP calculations the entire vibronic phase matrix was calculated directly from the fixed-nuclei matrices $\boldsymbol{\Phi}(\epsilon; R, r_0)$ via the usual adiabatic prescription.)

In the $0 \rightarrow 2$ cross section in figure 3, some minor differences are noticeable between the NADP, EMAP and BFVCC results, especially in regard to the position of the maximum and the amplitude of the partial cross section. Extensive formal and numerical consistency checks indicate that the small-scale structure in the $0 \rightarrow 2$ NADP cross section near 3.0 eV is not a numerical artefact. Rather, it may signal the presence in the NADP results of non-adiabatic effects, a suggestion supported by the different positions of the maxima in the BFVCC (fully non-adiabatic) and EMAP (fully adiabatic) cross sections. Such effects are not seen, however, in experimental data for this excitation (Allan 1985). Alternatively, this structure may be a consequence of our use of fixed-nuclei R-matrices based on Hartree–Fock electronic function for the target. Because the $v = 2$ vibrational wavefunction samples larger values of R than the $v = 1$ function does, an NADP calculation of the $0 \rightarrow 2$ cross section may overestimate the influence of the strong resonance at large R seen in figure 1, and hence may bring into play the well known deterioration of the Hartree–Fock Born–Oppenheimer potential curves as R increases towards dissociation. (In this regard we note that our resonance energy curves predict binding of H_2^- at $R \approx 2.6\ a_0$, a value smaller than those obtained in calculations based on a more sophisticated treatment of the target (McCurdy and Mowrey 1982, DeRose *et al* 1985).) In any case, non-adiabatic effects are evident in the cross sections for higher-lying excitations measured by Allan. Due to the difficulty of including values of $R > 2.5\ a_0$ in these calculations and our intention to abandon the Hartree–Fock potential energy curve in the next phase of this work, which will focus on dissociative attachment, we have not pursued the small structure in the $0 \rightarrow 2$ cross section further.

5. Conclusions

The essential question addressed in this paper is, how can one separate the mathematical description of the scattering into foreground and background parts in a way that is valid for all internuclear separations and that gives accurate, physically interpretable results? This question must be answered if one is to treat high-lying vibrational excitations or dissociative attachment within a continuum Born–Oppenheimer framework. A previous application to e–N_2 scattering (Grimm-Bosbach *et al* 1996) showed that the NADP method properly treats non-adiabatic effects for systems in which a physical resonance exists for all internuclear geometries relevant to the scattering process of interest. This paper extends that work to the more problematic case of systems in which the relevant geometries encompass radically different physical conditions, from unambiguous resonant scattering at large R to unambiguous non-resonant scattering at small R. We have demonstrated that the fixed-nuclei phase matrix evaluated at the boundary of the inner region can be separated for all R. The resulting procedure treats all internuclear separations on a common footing and leads to correct cross sections. The availability of benchmark BFVCC cross sections for e–H_2 scattering and the dramatic variation in the fixed-nuclei eigenphase sums (figure 1) make this an ideal system for calibrating the method.

The key equations of the present formulation are the definition (3) of the dimensionless fixed-nuclei phase matrix, the separation of this matrix into foreground and background parts evaluated by (6) and (7), the construction from these parts of the desired vibronic phase matrix (12), and the extraction in this construction of the free-electron phase matrix (15). The comparison of NADP vibrational cross sections for the $0 \rightarrow 1$ and $0 \rightarrow 2$ excitations

with those from benchmark BFVCC and fully adiabatic EMAP calculations validates this decomposition. This demonstration thus supports the applicability of the NADP method to the study of dissociative attachment in e–H$_2$ scattering, the ultimate goal of this research.

The essential computational device of the NADP method is the precursor potential energy curve in figure 2. This curve shows that the NADP method allows one to incorporate vibrational dynamics within a Born–Oppenheimer context consistently over the whole range of experimentally relevant internuclear separations. This formulation therefore liberates the theorist from the need to address imponderables such as, 'at which value of R do resonance effects become sufficiently unimportant that a non-reasonant adiabatic treatment (like the EMAP method) become appropriate?' The NADP method, with the free-electron phase matrix extracted as in section 3, simply, smoothly, and unambiguously merges with the fully adiabatic EMAP method with decreasing R, as shown in the cross section comparisons of figure 3.

To conclude, it is important to clarify the sense in which the NADP method is 'non-adiabatic'. The solution of the scattering problem in the inner region ($r < r_0$) is carried out entirely within the context of the Born–Oppenheimer approximation and hence is adiabatic, in that the electron–molecule wavefunction is approximated by a function that is separable in the vibrational coordinate of the nuclei and the electronic coordinates of the projectile (Schneider 1976). Non-adiabatic effects are introduced at r_0 in the construction of the foreground vibrational phase matrix (6) by means of the compete set $\{\chi_s(R)\}$, the eigenfunctions of $\hat{\mathcal{H}}^{(v)} + \epsilon_{\text{res}}(R, r_0)$ in equation (10). In the outer region $r > r_0$, non-adiabatic effects are fully taken into account through vibrational close-coupling in propagation of the vibronic R-matrix (13) into the asymptotic region.

Acknowledgments

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