SEMICLASSICAL WAVE PACKETS IN THE ANGLE REPRESENTATION AND THEIR ROLE IN MOLECULAR DYNAMICS

R.A. MARCUS

Noyes Laboratory of Chemical Physics [1], *California Institute of Technology, Pasadena, CA 91125, USA*

Received 11 August 1988; in final form 16 September 1988

Molecular wave packets generated by Gaussian optical pulses are discussed in the present paper. The systems treated either have pulses which are narrow relative to the width of the spectral absorption band or have molecules whose absorption band can be approximated by a Gaussian. One convenient approximate description is given, it is shown, by a semiclassical angle variable representation, which we used earlier in the treatment of inelastic molecular collisions. The results offer a relatively simple description of the motion of the packet, including its periods of oscillation, the time spent in various regions, and its extension in space at various times. The results are applied elsewhere to experimental data and to quantum mechanical calculations. The wave packet description is multidimensional.

1. Introduction

In recent observations of real-time dynamics in molecular systems a short optical pulse in the femtosecond regime has been used [1]. The resulting wave packet for the motion of the system on an upper electronic state arises from a convolution of the optical pulse and a function consisting of dipole operator acting on the initial molecular wavefunction. In the present paper we consider the ensuing molecular dynamics, treating first the one-dimensional case (section 2) and then extending the results to the multidimensional one (section 3). Because of the convolution, it should be noted, the width of the molecular wave packet moving on the upper surface just after the pulse can be considerably larger in coordinate space than that of the original wavefunction in the ground electronic state [2]. The relation of the width of the packet to that of the pulse and to that of the absorption spectrum is given in section 4.

For these systems we find it convenient to use the angle representation which we used earlier in the semiclassical theory of molecular collisions [3]. The properties of the resulting molecular wave packets can then (with a Gaussian distribution of energies) be relatively simple to treat in the first approximation. An application of some of the present results is given elsewhere, where an analysis of quantum mechanical and experimental results is made for the real-time oscillatory behavior of excited sodium halide molecules [2]. The present wave packets differ from packets which are Gaussian in ordinary space (or sums of the latter), treated by Heller and co-workers (ref. [4], and references therein). The difference is due, in part, to the different aims of the two calculations (section 5).

2. Theory

If an optical pulse is Gaussian shaped in time, as in the probability distribution $p(t)=\exp[-(t-t_0)^2/\sigma_t^2]$, the corresponding probability distribution in frequency space ν, $\bar{p}(\nu)$, determined from the Fourier transform of the amplitude function $\exp[-(t-t_0)^2/2\sigma_t^2-2\pi i\nu_L t]$, is proportional to $\exp[-h^2(\nu-\nu_L)^2/\sigma_L^2]$, where $\sigma_L=\hbar/\sigma_t$ and ν_L is the most probable optical frequency,

$$p(t)=\exp[-(t-t_0)^2/\sigma_t^2]\,,$$

$$\bar{p}(\nu)=\exp[-h^2(\nu-\nu_L)^2/\sigma_L^2]\,,\quad \sigma_L=\hbar/\sigma_t\,. \qquad (1)$$

[1] Contribution No. 7824.

When the spectral absorption envelope is sufficiently broad relative to the energy distribution in the optical pulse, as in the NaI case studied earlier [1,2], and when any detailed vibrational structure in the spectrum is neglected, the probability distribution of energies $P(E)$ of the molecular wave packet formed on the upper electronic state is also approximately a Gaussian, given by

$$P(E)=\exp[-(E-E_0)^2/\sigma_E^2]\,, \tag{2a}$$

where

$$\sigma_E=\hbar/\sigma_t=\sigma_L\,. \tag{2b}$$

More generally, when the absorption spectrum is not "white", but when it can be approximated by a Gaussian function of the frequency, eq. (2a) still applies, but with a σ_E given by an expression more general than eq. (2b) (section 4, eq. (26)).

We introduce molecular action–angle variables J and w that describe the exact motion (typically anharmonic) on the upper adiabatic surface [5]. In this angle representation an approximate eigenfunction for the Schrödinger equation is very simple (one reason for choosing this representation) [3]:

$$\Psi_n(w,t)=\exp(2\pi i n w-iE_n t/\hbar)\,, \tag{3}$$

where E_n is the eigenvalue. Ψ_n satisfies an approximate Schrödinger equation $H(J+\delta)\Psi_n=i\hbar\,\partial\Psi_n/\partial t$ [3]. Eq. (3) replaces the usual representation in ordinary space, which can involve Hermite polynomials, Laguerre polynomials, or more complicated wavefunctions. The angle variable w represents the phase of the molecular motion, while J is the classical analog of the quantum number n [5].

An unnormalized molecular wave packet for the molecular motion on the upper surface is next constructed from the eigenfunctions in eq. (3):

$$\Psi(w,t)=\sum_n \exp[-(E_n-E_{n0})^2/2\sigma_E^2+2\pi i n w-iE_n t/\hbar]\,, \tag{4}$$

where the E and E_0 in eq. (1) are now written equivalently as E_n and E_{n0}. To treat eq. (4), E_n-E_{n0} is first expanded in a series in $n-n_0$,

$$E-E_0\approx(J-J_0)\nu_0+\ldots=(n-n_0)h\nu_0+\ldots\,, \tag{5}$$

where n_0 is the most probable value of n and ν_0 denotes the molecular vibration frequency, $\partial E/\partial J$, evaluated at $J=J_0$. (There should be no danger of confusion of ν_0 with the most probable *optical* frequency ν_L in the pulse.) When the typical values of $|n-n_0|/n_0$ are small, the limits of $\pm\infty$ can be used for $n-n_0$. The sum in eq. (4) is next approximated by an integral. If the first-order expansion in eq. (5) is introduced for the E_n in the phase term $iE_nt/\hbar$ in eq. (4), integration shows that no spreading of the packet occurs. For spreading to occur a second-order expansion for the E_n in the $iE_nt/\hbar$ is needed,

$$E_n-E_{n0}\approx h\nu_0(n-n_0)+\tfrac{1}{2}h\nu_0'(n-n_0)^2+\ldots\,, \tag{6}$$

where $\nu_0'=\mathrm{d}\nu(n)/\mathrm{d}n$ evaluated at $n=n_0$. Integration of eq. (4) then yields

$$\Psi(w,t)=(2\pi\sigma_w^2)^{-1/2}\times\exp[-(w-\nu_0 t)^2/2\sigma_w^2+2\pi i n_0 w-iE_0 t/\hbar] \tag{7}$$

and

$$\sigma_w^2=(\hbar\nu_0/\sigma_E)^2+i\nu_0' t/2\pi\,. \tag{8}$$

We thus have for the unnormalized probability distribution of angle variables in the molecular wave packet,

$$|\Psi(w,t)|^2=(2\pi|\sigma_w|^2)^{-1}\exp[-(w-\nu_0 t)^2\,\mathrm{Re}(1/\sigma_w^2)]\,, \tag{9}$$

where Re denotes "real part of" and where

$$\mathrm{Re}(1/\sigma_w^2)=[(\hbar\nu_0/\sigma_E)^2+(\sigma_E\nu_0' t/h\nu_0)^2]^{-1}\,. \tag{10}$$

There are a number of consequences of eqs. (9) and (10). We first recall that in action–angle variables the interval (0, 1) for the angle variable covers one period of oscillation of the molecular motion. All values of w which differ by an integer correspond to the same value of the spatial coordinate [5]. For any time t in the prespreading time regime ($(\sigma_E\nu_0' t/h\nu_0)^2\ll 1$), the maximum of the probability distribution $|\Psi(w,t)|^2$ is seen from eq. (9) to occur at $w=\nu_0 t$. Thus, this maximum moves in angle space with a velocity $\dot{w}=\nu_0$. The packet oscillates, thereby, with a period $1/\nu_0$ equal to the classical period that corresponds semiclassically to the most probable quantum number n_0 in the packet.

The full width at half maximum Δw in angle space

during the prespreading time regime is a constant, equal to $2\sigma_w\sqrt{\ln 2}$, and in time space it is equal to $2\sigma_w\sqrt{\ln 2}/\nu_0$. Its fwhm in ordinary coordinate space Δx is then given in the first approximation by

$$\Delta x = 2\sqrt{\ln 2}\; v_x \sigma_w/\nu_0 \,, \tag{11a}$$

where v_x denotes the local classical velocity for the most probable energy E_{n0}.

When v_x is not constant over the interval Δx a more accurate conversion of σ_w to Δx in this prespreading regime is given by

$$\Delta x = 2\sqrt{\ln 2}\int v_x(w)\,\mathrm{d}w/\nu_0 = 2\sqrt{\ln 2}\int v_x\,\mathrm{d}t\,, \tag{11b}$$

where the integrals over w and t are over an interval σ_w and an interval σ_w/ν_0, respectively, each centered at the center of the wave packet. In the limit of a narrow wave packet eq. (11b) reduces to (11a).

3. Multidimensional case

When there are a number of coordinates, the eigenfunctions are again given by eq. (3), but with nw replaced by the sum $\sum_k n_k w_k$ [3]. The energy difference $E_n - E_{n0}$ can again be expanded as in eq. (5), but with the $(n-n_0)h\nu_0$ replaced by the sum $\sum_k (n_k - n_{0k})h\nu_{0k}$, where $\nu_{0k} = \partial E/\partial J_k$ evaluated at $J_k = J_{0k}$, and in the case of eq. (6) with the quadratic term becoming the sum $\sum_{kj} \frac{1}{2} h\nu_{jk}(n_j - n_{0j})(n_k - n_{0k})$, where ν_{jk} denotes

$$\nu_{jk} = (\partial^2 E/\partial n_j\,\partial n_k\, h)_0 \,. \tag{12}$$

The second derivative in eq. (12) is evaluated at the maximum, $n_k = n_{k0}$, for all k.

In this way the expression for the wave packet becomes, on introducing as variables $x_k = n_k - n_{0k}$,

$$\Psi(w,t) = \int\!\!\cdots\!\!\int_{-\infty}^{\infty} \exp\Big(-\sum a_{kj}x_k x_j + \mathrm{i}\sum b_k x_k\Big) \times \prod_k \mathrm{d}x_k \exp(\mathrm{i}\Phi)\,, \tag{13}$$

where a_{ij} is a symmetric complex-valued matrix $\mathbf{A}$ and the b_k can be regarded as components of a vector $\boldsymbol{b}$,

$$a_{jk} = h^2\nu_{0j}\nu_{0k}/2\sigma_E^2 - \pi\mathrm{i}\nu_{jk}t\,, \tag{14}$$

$$b_k = 2\pi(w_k - \nu_{0k}t)\,, \tag{15}$$

$$\Phi = 2\pi\sum n_{0k}w_k - E_0 t/\hbar\,. \tag{16}$$

The exponent in eq. (13) can be written as $-\boldsymbol{x}\cdot\mathbf{A}\boldsymbol{x} + \mathrm{i}\boldsymbol{b}\cdot\boldsymbol{x}$, where the dot denotes the scalar product and $\boldsymbol{x}$ is a vector with components x_k. This expression is equivalent to $-\boldsymbol{y}\cdot\mathbf{A}\boldsymbol{y} - \frac{1}{4}\boldsymbol{b}\cdot\mathbf{A}^{-1}\boldsymbol{b}$, where $\boldsymbol{y} = \boldsymbol{x} - \frac{1}{2}\mathrm{i}\mathbf{A}^{-1}\boldsymbol{b}$ and where we have used the fact that $\mathbf{A}$ (and hence $\mathbf{A}^{-1}$) equals its own transpose ($\mathbf{A}$ is a symmetric matrix). The integral over the y_k's is a standard one, and one finds

$$\Psi(w,t) = \pi^{N/2}(\det\mathbf{A})^{-1/2}\exp(-\tfrac{1}{4}\boldsymbol{b}\cdot\mathbf{A}^{-1}\boldsymbol{b} + \mathrm{i}\Phi)\,, \tag{17}$$

where N is the number of coordinates.

Thus, the exponent in the packet is a quadratic function of the b_k's and hence of the factors $w_k - \nu_k t$. The center of the packet thus moves with velocity components in angle space given by the ν_{0k}'s. The probability distribution in angle space is given by $|\Psi(w,t)|^2$,

$$|\Psi(w,t)|^2 = \pi^N |\det\mathbf{A}|^{-1}\exp(-\tfrac{1}{2}\mathrm{Re}\,\boldsymbol{b}\cdot\mathbf{A}^{-1}\boldsymbol{b})\,. \tag{18}$$

In the multidimensional case the packet can be regarded as having an N-dimensional elliptical cross section and so has N "principal widths" along the principal axes of this cross section. The $1/\sigma^2$'s for these widths are the real parts of the eigenvalues of the matrix of coefficients of the factors $w_k - \nu_{0k}t$ there, i.e. of $\frac{1}{2}(2\pi)^2\mathbf{A}^{-1}$.

4. Energy distribution and its relation to pulse and absorption widths

We next obtain an expression for the σ_E in eq. (2a), namely eq. (26) below. The latter reduces to eq. (2b) when the width of the absorption spectrum is large relative to that of the optical pulse. We consider the optical excitation of a molecule from one electronic state to the upper state, the transition being induced by an electric field $\boldsymbol{E}(t)$,

$$\boldsymbol{E}(t) = \boldsymbol{E}_0\exp(-\mathrm{i}\omega_{\mathrm{L}}t - t^2/2\sigma_t^2) + \mathrm{c.c.}, \quad t \geqslant -t_0\,, \tag{19}$$

where $\omega_{\mathrm{L}}/2\pi$ $(=\nu_{\mathrm{L}})$ is the mean optical frequency of the pulse. Using first-order perturbation theory for the optical–molecular interaction, the molecular

wavefunction $\Psi(t)$ for the resulting nuclear motion in the upper electronic state is given by [2,6]

$$\Psi(t)=(\mathrm{i}/\hbar)\int_{-t_0}^{t}\mathrm{d}\tau\exp[-\mathrm{i}H(t-\tau)/\hbar]$$

$$\times\boldsymbol{\mu}\cdot\boldsymbol{E}(\tau)\Phi_i\exp(-\mathrm{i}E_i\tau/\hbar)\,, \qquad (20)$$

where H is the Hamiltonian for the nuclear motion on the upper electronic state, $\boldsymbol{\mu}$ is the transition dipole moment operator, and $\Phi_i\exp(-\mathrm{i}E_it/\hbar)$ is the molecular wavefunction for the initial electronic state.

We consider the behavior at some time after the pulse has effectively ceased. In effect, the upper limit in eq. (20) can then be replaced by $+\infty$. The lower limit was effectively $-\infty$. The eigenfunctions Ψ_n of H are given by eq. (3). H acting on $\exp(2\pi\mathrm{i}nw)$ yields $E_n\exp(2\pi\mathrm{i}nw)$ [3]. The projection of $\boldsymbol{\mu}$ along $\boldsymbol{E}_0$ is denoted by μ_E. If μ_E acting on the ground-state wavefunction Φ_i is expanded in the eigenfunctions of the upper state,

$$\mu_E\Phi_i(w)=\sum_n f_n\exp(2\pi\mathrm{i}nw)\,, \qquad (21)$$

we then have

$$\Psi(w,t)=(E^0/\mathrm{i}\hbar)\sum_n f_n\exp(-\mathrm{i}E_nt/\hbar)\exp(2\pi\mathrm{i}nw)$$

$$\times\int_{-\infty}^{\infty}\exp[\mathrm{i}(E_n-E_i-\hbar\omega_\mathrm{L})\tau/\hbar]$$

$$\times\exp(-\tau^2/2\sigma_t^2)\,\mathrm{d}\tau\,, \qquad (22)$$

where E^0 is the amplitude of $\boldsymbol{E}_0$ (not to be confused with the E_0 in eq. (2)).

Parenthetically we note that eq. (21) and its time-dependent counterpart (the same as eq. (21), but with an additional factor $\exp(-\mathrm{i}E_it/\hbar)$ on the left- and $\exp(-\mathrm{i}E_nt/\hbar)$ on the right-hand side), can be introduced into a time-correlation function, e.g. ref. [4], for $\epsilon(\omega)/\omega$, where $\epsilon(\omega)$ is the absorbance. This $\epsilon(\omega)/\omega$ is found, thereby, to be proportional to the usual $\sum_n|f_n|^2\delta(E_n-E_i-\hbar\omega)$, and so to $|f_n|^2$ summed over n's with $(E_n-E_i)/\hbar$ in a small interval $(\omega,\,\omega+\Delta\omega)$.

Integration over τ in eq. (22) yields

$$\Psi(w,t)=(E^0/\mathrm{i}\hbar)\sigma_t\sqrt{2\pi}\sum_n f_n\exp(-\mathrm{i}E_nt/\hbar)$$

$$\times\exp[-(E_n-E_i-\hbar\omega_\mathrm{L})^2/2\sigma_\mathrm{L}^2]\exp(2\pi\mathrm{i}nw)\,, \qquad (23)$$

where $\sigma_\mathrm{L}=\hbar/\sigma_t$ (eq. (1)).

The $|f_n|^2$ has a maximum $n=n_\mathrm{a}$, at an energy E_{n_a}, which corresponds to the maximum in the absorption spectrum (or really in $\epsilon(\omega)/\omega$):

$$E_{n_\mathrm{a}}-E_i=\hbar\omega_\mathrm{L}^{\max}\,, \qquad (24)$$

where $\omega_\mathrm{L}^{\max}/2\pi$ is the frequency of light at the absorption maximum.

We next approximate the shape of the "reduced" absorbance $\epsilon(\omega)/\omega$, and hence of $|f_n|^2$ by a Gaussian:

$$|f_n|^2=\exp[-(E_n-E_{n_\mathrm{a}})^2/\sigma_\mathrm{a}^2]\,. \qquad (25)$$

We take f_n as real (it is for a non-degenerate vibration) and let the maximum of $f_n\exp[-(E_n-E_i-\hbar\omega_\mathrm{L})^2/2\sigma_\mathrm{L}^2]$ occur at some $n=n_0$.

The distribution of energies E_n, $P(E_n)$, arising from eqs. (23) and (25) is the same as in eq. (2a), with E and E_0 replaced by E_n and E_{n0} now given by

$$\frac{1}{\sigma_E^2}=\frac{1}{\sigma_\mathrm{a}^2}+\frac{1}{\sigma_\mathrm{L}^2} \qquad (26)$$

and

$$E_{n0}=E_{n_\mathrm{a}}+(\sigma_E\Delta\hbar\omega_\mathrm{L}/\sigma_\mathrm{L})^2\,. \qquad (27)$$

Here, $\Delta\omega_\mathrm{L}/2\pi$ is the off-resonance frequency

$$\Delta\omega_\mathrm{L}=\omega_\mathrm{L}-\omega_\mathrm{L}^{\max}\,. \qquad (28)$$

Eq. (23) thus yields

$$\Psi(w,t)=\Psi(w,t)_{\mathrm{eq.\,(4)}}(E^0/\mathrm{i}\hbar)\sigma_t\sqrt{2\pi}$$

$$\times\exp[-(\Delta\hbar\omega_\mathrm{L})^2/2\bar{\sigma}^2]\,, \qquad (29)$$

where

$$\bar{\sigma}^2=\sigma_\mathrm{a}^2+\sigma_\mathrm{L}^2 \qquad (30)$$

and where the σ_E in eq. (4) is given by eq. (26). Eqs. (26) and (29) are the desired results of this section.

The $\bar{\sigma}^2$ in the attenuation factor in eqs. (29) and (30) is the expected one: in the overlap in eqs. (23)–(25) of two Gaussian energy distributions the standard result is obtained that the total σ^2 is the sum of the two σ^2's. In eq. (26) the expected limits of σ_E^2 are also obtained: When the absorption spectrum has

a sufficiently large width σ_a ("white spectrum"), the energy width σ_E of the molecular wave packet reduces to that of the optical pulse, σ_L, as in eq. (2b). At the other limit, when σ_L is sufficiently large ("white" pulse) σ_E is seen from (26) to reduce to σ_a.

In the multidimensional case, eq. (23) can again be used, but with the $2\pi nw$ replaced by $\sum_k 2\pi n_k w_k$. Thereby, eq. (17) is again obtained with the additional multiplicative factor contained in eq. (29). The μ_E in eq. (21) is a function of the orientational w_k's and (except in a Condon approximation) the vibrational w_k's.

5. Discussion

We consider several miscellaneous aspects of the present formulation. In ref. [2] a quantum mechanical analysis of the time behavior of the NaI system a one-dimensional (radial coordinate) treatment of the vibration was made, and some of the results were interpreted semiclassically with the present expressions. These applications included the use of eq. (11a), as well as an estimate of aspects such as vibrational and centrifugal rotational effects on the oscillation frequency of the packet [2]. The width of the packet in ref. [2] showed reasonable agreement with eq. (11a) for fixed x, for different optical pulse times. It can also be seen from (11a) that as x is varied the width Δx is expected to change, even when Δw is constant: When v_x decreases, for example, in a region where the potential energy approaches E_{n0}, Δx is also expected to decrease, and in proportion to v_x. An example of this behavior was found in ref. [2]: A narrowing of the NaI wave packet occurred after it moved from its covalent to its ionic form on the upper adiabatic curve [2], and the extent of narrowing was consistent with eq. (11a). (The wave packet has a complicated behavior, however, when the potential energy curve is steep near the classical turning point [2].)

In a system such as NaI, where an avoided crossing of two diabatic potential curves occurs near some point x_0 and the system moves mainly on the upper adiabatic curve, it spends part of its time essentially on one of the diabatic curves (on one side of the avoided crossing) and part of the time on the other. The time spent on the covalent part was determined by direct real-time off-resonant spectroscopic observation [1]. This time is simply $2\int dx/v_x$, where the integral is from relevant classical turning point to x_0. The total period of the motion is obtained by integrating $2\int dx/v_x$ between the two classical turning points. This result was applied in ref. [2].

Since the present analysis is multidimensional it can be also used to treat systems with more coordinates than those in NaI, provided the quantum mechanical motion is "quasi-periodic", i.e. provided an approximate action–angle quantum mechanical description can be used. Incidentally, even where the classical motion is chaotic rather than quasi-periodic, the chaos is sometimes on a small enough scale locally that the quantum system still retains fairly well the regular sequences of energy levels expected for a "quasi-periodic" system [7,8] (few "overlapping avoided crossings" [7]).

The quantum number n in eq. (4) is an integer, enabling the wavefunction to be single-valued. In eq. (4) the distribution of n's is presumed to be sufficiently broad that a continuous distribution for n can be used. There results no difficulty with single-valuedness of the wavefunction in eq. (7) provided the w in the $w-v_0t$ is understood to be such that $w-v_0t$ is chosen to lie in the unit interval. As noted earlier all values of w mod an integer correspond to the same point in ordinary coordinate space [5], and the above choice for the w appearing in eq. (7) is clear from the results $\dot{w}=v_0$.

One question which we plan to explore concerns the conditions under which the expansion for $E-E_0$ in eq. (5) suffices for calculating the probability distribution of n's, whereas in treating the complex-valued quantity $iEt/\hbar$ the next term in the expansion was also used (eq. (6)). The latter term affects only the spreading, so that the use of eq. (2) for both purposes would be appropriate before significant spreading occurs. Regardless, however, eqs. (7) and (8) remain a valid description for spreading also, when the molecular wave packet in eq. (4) can be regarded as having an initial Gaussian distribution in quantum-number space for motion on the given adiabatic potential energy surface.

In one wave packet, a minimum uncertainty wave packet constructed from harmonic oscillator wave-

functions, the distribution in quantum number space which appears in the amplitude is $a^n/\sqrt{n!}$ (a sum over such n's is used, rather than an integral), [9]. When the n's involved are sufficiently large this distribution of amplitudes, too, can be expressed as a Gaussian function of $n-n_0$. The lack of spreading in a harmonic oscillator potential well is then reflected in eqs. (9) and (10), since ν'_0 is now zero for that potential.

The main focus in the present paper and in ref. [2] is on experiments involving the real-time observation of the dynamics of molecular wave packets. When, instead, the problem of particular interest is the calculation of time-independent properties such as absorption spectra [4], the "optical pulse" used is one which is so long that the study of the dynamics involves that of the wavefunction $\mu_E \Phi_i$, itself, moving on the upper potential energy surface, as in ref. [4]. As noted in section 1 and can be seen from section 4, this wavefunction is typically much narrower than that involved in real-time observations associated with, say, a 50 fs optical pulse.

It will be interesting to see the development of this interplay between the femtosecond real-time measurements and the high-resolution longer time spectroscopic techniques. An example of the interplay is seen in ref. [1].

Acknowledgement

It is a pleasure to acknowledge the support of this research by the National Science Foundation, and to acknowledge helpful discussions with Professor Ahmed Zewail on the experiments and with Professor Horia Metiu on the quantum calculations.

References

[1] M.J. Rosker, T.S. Rose and A.H. Zewail, Chem. Phys. Letters 146 (1988) 175;
T.S. Rose, M.J. Rosker and A.H. Zewail, J. Chem. Phys. 88 (1988) 6672, and references therein.

[2] V. Engel, H. Metiu, R. Almeida, R.A. Marcus and A.H. Zewail, Chem. Phys. Letters 152 (1988) 1.

[3] R.A. Marcus, Chem. Phys. Letters 7 (1970) 525; J. Chem. Phys. 54 (1971) 3965;
J.H. Van Vleck, Proc. Natl. Acad. Sci. US 14 (1928) 178.

[4] E.J. Heller, Accounts Chem. Res. 74 (1981) 368;
D.J. Tannor and E.J. Heller, J. Chem. Phys. 77 (1982) 202;
D. Huber and E.J. Heller, J. Chem. Phys. 87 (1987) 5302.

[5] M. Born, The mechanics of the atom (Ungar, New York, 1960);
H.C. Corben and P. Stehle, Classical mechanics, 2nd Ed. (Wiley, New York, 1960);
R.A. Marcus, J. Chem. Phys. 45 (1966) 4500.

[6] S.Y. Lee and E.J. Heller, J. Chem. Phys. 71 (1979) 4777;
R. Loudon, The quantum theory of light, 2nd Ed. (Clarendon Press, Oxford, 1983) pp. 193, 194;
J.J. Sakurai, Advanced quantum mechanics (Addison-Wesley, Reading, 1957) p. 183.

[7] D.W. Noid, M.L. Koszykowski, M. Tabor and R.A. Marcus, J. Chem. Phys. 72 (1980) 6169;
R.A. Marcus, Faraday Discussions Chem. Soc. 75 (1983) 103, and references therein.

[8] M.V. Berry, Ann. Phys. 131 (1981) 163;
D.W. Noid, M.L. Koszykowsky and R.A. Marcus, Ann. Rev. Phys. Chem. 32 (1981) 267;
M.V. Shuryak, Soviet Phys. JETP 36 (1976) 1;
M.V. Berry, Am. Inst. Phys. Conf. Proc. 46 (1978) 115;
K.G. Kay, J. Chem. Phys. 72 (1980) 5955.

[9] L.I. Schiff, Quantum mechanics, 3rd Ed. (McGraw-Hill, New York, 1968) p. 75.