Quantum Theory of Molecular Photodissociation

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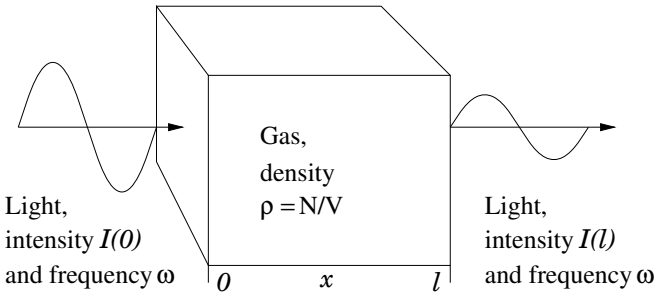
Contents

1 Light Absorption by Molecules

Recall the Beer-Lambert Law:

$$I(\ell) = I(0)\, e^{-\sigma(\omega)\rho\ell}$$

where



and $\sigma(\omega)$ is a frequency-dependent molecular absorption cross section (with the dimensions of an area).

In this lecture we will develop a microscopic theory for $\sigma(\omega)$ by considering the interaction of the light (treated as a classical electromagnetic wave) with a single gas molecule (treated quantum mechanically) [1].

1.1 Time-dependent perturbation theory

Consider a molecule with internal Hamiltonian $H^{(0)}$ and orthonormal eigenstates $|\psi_n\rangle$ (supposed for the moment to be discrete):

$$H^{(0)}\,|\,\psi_n\rangle = E_n\,|\,\psi_n\rangle \tag{1.1}$$

where

$$\langle\psi_m\,|\,\psi_n\rangle = \delta_{mn} \tag{1.2}$$

and

$$\sum_n |\,\psi_n\rangle\,\langle\psi_n\,| = 1. \tag{1.3}$$

The corresponding time-dependent states

$$|\,\Psi_n(t)\rangle = e^{-iE_nt/\hbar}\,|\,\psi_n\rangle \tag{1.4}$$

satisfy

$$i\hbar \frac{d}{dt} \mid \Psi_n(t)\rangle = H^{(0)} \mid \Psi_n(t)\rangle \tag{1.5}$$

and

$$\langle \Psi_m(t) \mid \Psi_n(t)\rangle = \delta_{mn} \tag{1.6}$$

and

$$\sum_n \mid \Psi_n(t)\rangle \langle \Psi_n(t) \mid = 1. \tag{1.7}$$

Now subject the molecule to a perturbation $\lambda H^{(1)}(t)$, so that

$$i\hbar \frac{d}{dt} \mid \Psi(t)\rangle = H(t) \mid \Psi(t)\rangle \tag{1.8}$$

with

$$H(t) = H^{(0)} + \lambda H^{(1)}(t), \tag{1.9}$$

and let

$$\mid \Psi(t)\rangle = \sum_n \mid \Psi_n(t)\rangle \, a_n(t) \tag{1.10}$$

where $a_n(t) = \langle \Psi_n(t) \mid \Psi(t)\rangle$ is the amplitude (and $P_n(t) = \mid a_n(t) \mid^2$ is the probability) for the molecule to be found in the state $\mid \Psi_n(t)\rangle$ at time t.

It is straightforward to show that eqs. (1.5) to (1.10) imply the following evolution equation for the amplitudes $a_m(t)$:

$$i\hbar \, \dot{a}_m(t) = \lambda \sum_n H^{(1)}_{mn}(t) \, a_n(t) \tag{1.11}$$

where

$$H^{(1)}_{mn}(t) = \langle \Psi_m(t) \mid \, H^{(1)}(t) \, \mid \Psi_n(t)\rangle \, . \tag{1.12}$$

This evolution equation is still exact, but it is generally very difficult to solve exactly. The standard approach is therefore to assume that λ is small and solve it by time-dependent perturbation theory.

Thus, we set

$$a_m(t) = a^{(0)}_m(t) + \lambda \, a^{(1)}_m(t) + \lambda^2 \, a^{(2)}_m(t) + \cdots \tag{1.13}$$

and require that eq. (1.11) is satisfied to each consecutive order in λ:

$$\lambda^0 : \qquad i\hbar \, \dot{a}^{(0)}_m(t) = 0 \tag{1.14}$$

$$\lambda^1 : \qquad i\hbar \, \dot{a}^{(1)}_m(t) = \sum_n H^{(1)}_{mn}(t) \, a^{(0)}_n(t) \tag{1.15}$$

(etc.) Equation (1.14) integrates to give $a_m^{(0)}(t) =$ constant, which is most conveniently chosen to be $a_m(t=0)$:

$$a_m^{(0)}(t) = a_m(0). \tag{1.16}$$

This choice implies $a_m^{(1)}(0) = 0$, and eq. (1.15) therefore integrates to give

$$a_m^{(1)}(t) = -\frac{i}{\hbar}\sum_n \int_0^t H_{mn}^{(1)}(t')\, a_n(0)\, dt' \tag{1.17}$$

Combining eqs. (1.13), (1.16) and (1.17) gives

$$a_m(t) = a_m(0) - \frac{i}{\hbar}\sum_n \int_0^t \lambda H_{mn}^{(1)}(t')\, a_n(0)\, dt' \tag{1.18}$$

to first order in the perturbation parameter λ.

Finally, suppose that the perturbation $\lambda H^{(1)}(t)$ is switched on at time $t = 0$ when only one initial quantum state $n = i$ of the unperturbed molecule is populated with amplitude $a_i(0) = 1$. Equation (1.18) simplifies under these circumstances to give the amplitude in each final quantum state $m = f \neq i$ at time t as

$$a_{fi}(t) = -\frac{i}{\hbar}\int_0^t \lambda H_{fi}^{(1)}(t')\, dt'. \tag{1.19}$$

1.2 Classical electromagnetic radiation

A classical electromagnetic wave is a solution of Maxwell's equations in free space [2]

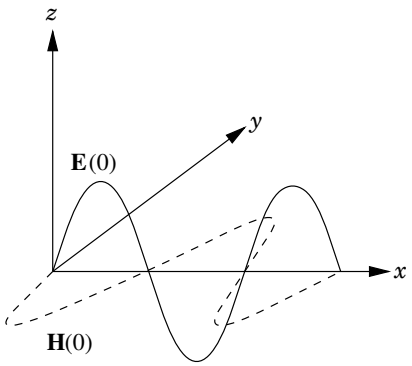
$$\nabla \cdot \mathbf{E}(t) = 0 \tag{1.20}$$

$$\nabla \wedge \mathbf{E}(t) = -\mu_0 \frac{\partial \mathbf{H}(t)}{\partial t} \tag{1.21}$$

$$\nabla \cdot \mathbf{H}(t) = 0 \tag{1.22}$$

$$\nabla \wedge \mathbf{H}(t) = +\epsilon_0 \frac{\partial \mathbf{E}(t)}{\partial t} \tag{1.23}$$

where $\mathbf{E}(t)$ is the electric field strength (in Vm^{-1}), $\mathbf{H}(t)$ is the magnetic field strength (in Am^{-1}), ϵ_0 is the vacuum permittivity and μ_0 is the vacuum permeability ($\epsilon_0\mu_0 = 1/c^2$).



For simplicity, we shall take the incident light to be a plane-polarised electromagnetic wave propagating along the laboratory x axis with its electric field vector in the $+z$ direction and its magnetic field vector in the $-y$ direction as shown in the diagram above:

$$\mathbf{E}(t) = +E_0 \sin(kx - \omega t)\mathbf{k} \tag{1.24}$$

$$\mathbf{H}(t) = -H_0 \sin(kx - \omega t)\mathbf{j}. \tag{1.25}$$

This wave clearly satisfies eqs. (1.20) and (1.22). The fact that it must also satisfy eq. (1.21) implies

$$kE_0 = \mu_0 \omega H_0 \tag{1.26}$$

and the fact that it must satisfy eq. (1.23) implies

$$kH_0 = \epsilon_0 \omega E_0 \tag{1.27}$$

which can be rearranged to give

$$k = \omega\sqrt{\epsilon_0 \mu_0} = \omega/c \tag{1.28}$$

and

$$\epsilon_0 E_0^2 = \mu_0 H_0^2. \tag{1.29}$$

E_0 and H_0 are thus related, and the wavelength of the light is $\lambda = 2\pi/k = 2\pi c/\omega = c/\nu$.

In order to make the connection with the Beer-Lambert Law we shall also need to know the intensity I of the light. This is defined as the electromagnetic energy passing through unit area in unit time, and is therefore related to the average energy density (or energy per unit volume) W of the light by

$$I = cW. \tag{1.30}$$

According to electromagnetic theory [2], the energy density of an electric field $\mathbf{E}$ is $W_E = \frac{1}{2}\epsilon_0 E^2$ and the energy density of a magnetic field $\mathbf{H}$ is $W_H = \frac{1}{2}\mu_0 H^2$. For the sinusoidal electric and magnetic fields in eqs. (1.24) and (1.25) we simply average these energy densities over a period of oscillation:

$$W_E = \frac{1}{2}\epsilon_0 E_0^2 \times \frac{\omega}{2\pi}\int_0^{2\pi/\omega} \sin^2(kx - \omega t)\, dt = \frac{1}{4}\epsilon_0 E_0^2 \tag{1.31}$$

$$W_H = \frac{1}{2}\mu_0 H_0^2 \times \frac{\omega}{2\pi}\int_0^{2\pi/\omega} \sin^2(kx - \omega t)\, dt = \frac{1}{4}\mu_0 H_0^2. \tag{1.32}$$

The average energy density of the light in eqs. (1.24) and (1.25) is thus

$$W = W_E + W_H = \frac{1}{4}\epsilon_0 E_0^2 + \frac{1}{4}\mu_0 H_0^2 = \frac{1}{2}\epsilon_0 E_0^2. \tag{1.33}$$

1.3 The electric dipole interaction

The dominant light-molecule interaction is usually the electric dipole interaction

$$\mu \cdot \mathbf{E}(t) = \mu_z E_0 \sin(kx - \omega t) \tag{1.34}$$

where

$$\mu = e\sum_I Z_I \mathbf{R}_I - e\sum_i \mathbf{r}_i \tag{1.35}$$

is the total (nuclear and electronic) dipole moment operator of the molecule and $\mathbf{E}(t)$ is the electric field of the light.

As it stands, however, we cannot use $\mu \cdot \mathbf{E}(t)$ directly as our perturbation Hamiltonian $\lambda H^{(1)}(t)$, because the perturbation Hamiltonian operates on the internal (centre-of-mass) coordinates of the molecule whereas the electric field $\mathbf{E}(t)$ in eq. (1.34) depends on laboratory coordinates relative to axes fixed in space. The way around this difficulty is to consider how the electric dipole interaction affects the molecular translational eigenstates [3]

$$\langle \overline{\mathbf{r}} \,|\, \mathbf{p} \rangle = h^{-3/2} e^{+i\mathbf{p}\cdot\overline{\mathbf{r}}/\hbar} \tag{1.36}$$

where $\mathbf{p}$ and $\overline{\mathbf{r}}$ are the molecular momentum and centre-of-mass.

In particular, eqs. (1.34) and (1.36) lead us to consider the matrix element

$$\langle \mathbf{p}_f \mid \mu \cdot \mathbf{E}(t) \mid \mathbf{p}_i \rangle = \frac{1}{h^3} \int e^{-i\mathbf{p}_f \cdot \overline{\mathbf{r}}/\hbar}\, \mu_z\, E_0\, \sin(kx - \omega t)\, e^{+i\mathbf{p}_i \cdot \overline{\mathbf{r}}/\hbar}\, d\overline{\mathbf{r}} \quad (1.37)$$

which can be evaluated by the following argument. Firstly, the dipole moment operator μ_z is independent of the centre-of-mass vector $\overline{\mathbf{r}}$ for a neutral molecule and can therefore be taken outside the integral. Secondly, the wavelength λ of the light is usually *much* larger than the length of a typical molecule (eg: the UV/visible borderline is at 4000Å, whereas a typical molecular dimension might be 4Å). The molecule therefore only effectively sees a constant electric field from the light at any instant, corresponding to the electric field at the molecular centre-of-mass, and the x in the integrand of eq. (1.37) can therefore be replaced to a good approximation by the x-component $\overline{x}$ of $\overline{\mathbf{r}}$. With these simplifications in hand, the matrix element can be evaluated to give

$$\begin{aligned}
\langle \mathbf{p}_f \mid \mu \cdot \mathbf{E}(t) \mid \mathbf{p}_i \rangle &= \frac{\mu_z\, E_0}{h^3} \int e^{-i\mathbf{p}_f \cdot \overline{\mathbf{r}}/\hbar}\, \sin(k\overline{x} - \omega t)\, e^{+i\mathbf{p}_i \cdot \overline{\mathbf{r}}/\hbar}\, d\overline{\mathbf{r}} \\
&= \frac{\mu_z\, E_0}{2ih^3} \int e^{-i\mathbf{p}_f \cdot \overline{\mathbf{r}}/\hbar + i(k\overline{x} - \omega t) + i\mathbf{p}_i \cdot \overline{\mathbf{r}}/\hbar} - e^{-i\mathbf{p}_f \cdot \overline{\mathbf{r}}/\hbar - i(k\overline{x} - \omega t) + i\mathbf{p}_i \cdot \overline{\mathbf{r}}/\hbar}\, d\overline{\mathbf{r}} \\
&= \frac{\mu_z\, E_0}{2i} \left[e^{-i\omega t}\, \delta(\mathbf{p}_f - \mathbf{p}_i - \mathbf{p}_k) - e^{+i\omega t}\, \delta(\mathbf{p}_f - \mathbf{p}_i + \mathbf{p}_k) \right] \qquad (1.38)
\end{aligned}$$

where $\mathbf{p}_k = \hbar k\, \mathbf{i} \equiv h/\lambda \mathbf{i}$ is the de Broglie momentum of the light and the last line follows from the normalisation of the translational wavefunctions in eq. (1.36) [3]:

$$\langle \mathbf{p}' \mid \mathbf{p} \rangle = \delta(\mathbf{p}' - \mathbf{p}). \quad (1.39)$$

Equation (1.38) has a clear interpretation. Either the molecule can absorb light as a result of the $\mu \cdot \mathbf{E}(t)$ interaction, in which case its final momentum is $\mathbf{p}_f = \mathbf{p}_i + \mathbf{p}_k$ and the appropriate internal coordinate perturbation Hamiltonian is

$$\lambda H^{(1)}(t) = +\frac{\mu_z\, E_0}{2i} e^{-i\omega t} \quad (1.40)$$

or else it can emit light (by stimulated emission), in which case its final momentum is $\mathbf{p}_f = \mathbf{p}_i - \mathbf{p}_k$ and the appropriate internal coordinate perturbation Hamiltonian is

$$\lambda H^{(1)}(t) = -\frac{\mu_z\, E_0}{2i} e^{+i\omega t}. \quad (1.41)$$

Momentum is conserved either way, provided that the momentum of the absorbed or emitted light is given by the de Broglie relation $p = h/\lambda$ (which we know to be true for photons, even though the classical electromagnetic wave which we have used to derive eq. (1.38) is not quantised and does not contain any reference to h).

(The momentum transfer from the light to the molecule in eq. (1.38) has a comparatively small effect, because the momentum of the light is typically several orders of magnitude smaller than the momentum of the molecule. It is nevertheless observable with intense enough radiation, and it forms the basis of laser cooling in atomic traps.)

1.4 Fermi's Golden Rule

We can now confine our attention exclusively to absorption and substitute the appropriate perturbation Hamiltonian $\lambda H^{(1)}(t)$ from eq. (1.40) into eq. (1.12) (with the replacements $m \to f$ and $n \to i$ as in eq. (1.19)) to give

$$\lambda H_{fi}^{(1)}(t) = \frac{E_0}{2i} \langle \Psi_f(t) \mid \mu_z \mid \Psi_i(t) \rangle \; e^{-i\omega t} = \frac{E_0 \, M_{fi}}{2i} \, e^{+i(\omega_{fi} - \omega)t} \tag{1.42}$$

where

$$M_{fi} = \langle \psi_f \mid \mu_z \mid \psi_i \rangle \tag{1.43}$$

is the electric dipole transition matrix element between the initial and final quantum states $\mid \psi_i \rangle$ and $\mid \psi_f \rangle$ and $\omega_{fi} = (E_f - E_i)/\hbar$ is the corresponding transition frequency.

Substituting eq. (1.42) into eq. (1.19) gives the amplitude of the wavefunction in the final quantum state f at time t as

$$\begin{aligned} a_{fi}(t) &= -\frac{i}{\hbar} \int_0^t \lambda H_{fi}^{(1)}(t') \, dt' \\ &= -\frac{E_0 \, M_{fi}}{2\hbar} \int_0^t e^{+i(\omega_{fi} - \omega)t'} \, dt' \\ &= -\frac{E_0 \, M_{fi}}{2i\hbar} \frac{e^{+i(\omega_{fi} - \omega)t} - 1}{(\omega_{fi} - \omega)}. \end{aligned} \tag{1.44}$$

The probability that the final quantum state will be populated at time t is therefore

$$P_{fi}(t) = \mid a_{fi}(t) \mid^2 = \frac{E_0^2 \mid M_{fi} \mid^2}{2\hbar^2} \frac{1 - \cos(\omega_{fi} - \omega)t}{(\omega_{fi} - \omega)^2} \tag{1.45}$$

and the rate of population of the final quantum state is

$$k_{fi}(t) = \frac{d}{dt} P_{fi}(t) = \frac{E_0^2 \mid M_{fi} \mid^2}{2\hbar^2} \frac{\sin(\omega_{fi} - \omega)t}{(\omega_{fi} - \omega)}. \tag{1.46}$$

As time passes, the right-hand-side of this equation becomes increasingly peaked around $\omega_{fi} - \omega = 0$, and only the resonant transition $\omega = \omega_{fi}$ prevails (just as one would expect to see experimentally). The long-time limit of eq. (1.46) is therefore particularly important, and this is given by

$$\begin{aligned} k_{fi} &= \lim_{t \to \infty} k_{fi}(t) \\ &= \frac{E_0^2 \mid M_{fi} \mid^2}{2\hbar^2} \lim_{t \to \infty} \frac{\sin(\omega_{fi} - \omega)t}{(\omega_{fi} - \omega)} \\ &= \frac{E_0^2 \mid M_{fi} \mid^2}{2\hbar^2} \pi \, \delta(\omega_{fi} - \omega). \end{aligned} \tag{1.47}$$

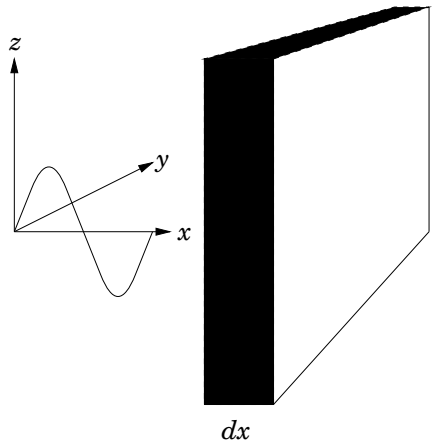
Equation (1.47) is Fermi's Golden Rule for the asymptotic ($t \to \infty$) transition rate k_{fi} [4]. All that remains is to convert this into an expression for the molecular absorption cross section $\sigma(\omega)$ and hence derive the Beer-Lambert Law.

1.5 The absorption cross section

The first step in this direction is to use eqs. (1.30) and (1.33) to eliminate E_0 from eq. (1.47) in favour of the intensity I of the light:

$$k_{fi} = \frac{\pi I \mid M_{fi} \mid^2}{\hbar^2 \epsilon_0 \, c} \, \delta(\omega_{fi} - \omega). \tag{1.48}$$

Now consider the absorption of radiation with angular frequency ω by a thin slice of the gas with thickness dx perpendicular to the direction of propagation:



The decrease in the intensity (energy per unit area per unit time) of the light due to absorption by the molecules in the slice is given by

$$dI = -c\rho \sum_f \hbar\omega_{fi}\, k_{fi}\, dt = -\rho \sum_f \hbar\omega_{fi}\, k_{fi}\, dx \tag{1.49}$$

where $\rho = N/V$ is the number density of molecules in the slice, $\hbar\omega_{fi} = E_f - E_i$ is the energy absorbed per molecule due to the transition from $|\,\psi_i\rangle$ to $|\,\psi_f\rangle$, and $k_{fi}\,dt$ is the probability that a given molecule will make this transition in a time interval $dt = dx/c$.

Dividing eq. (1.49) by dx and making use of Fermi's Golden Rule for k_{fi} gives

$$\begin{aligned}
\frac{dI}{dx} &= -\rho \sum_f \hbar\omega_{fi}\, k_{fi} \\
&= -\frac{\rho\pi I}{\hbar\epsilon_0\, c} \sum_f \omega_{fi}\, \delta(\omega_{fi} - \omega)\, |\, M_{fi}\,|^2 \\
&= -\frac{\rho\pi I}{\hbar\epsilon_0\, c} \sum_f \omega\, \delta(\omega - \omega_{fi})\, |\, M_{fi}\,|^2 \\
&= -\sigma_i(\omega)\rho I
\end{aligned} \tag{1.50}$$

where

$$\sigma_i(\omega) = \frac{\pi\omega}{\hbar\epsilon_0 c} \sum_f \delta(\omega - \omega_{fi})\, |\, M_{fi}\,|^2 \tag{1.51}$$

is the absorption cross section from the initial quantum state $|\psi_i\rangle$.

Equation (1.50) is the differential form of the Beer-Lambert Law

$$I(\ell) = I(0)e^{-\sigma(\omega)\rho\ell} \tag{1.52}$$

and so completes what we have set out to do. We shall therefore end this lecture by summarising the approximations that went into its derivation:

1. The light-molecule interaction has been treated by first-order perturbation theory (which will be valid provided the radiation is not too intense).

2. The light has been treated as a classical electromagnetic wave (which is known to give the right result for absorption and stimulated emission, although it completely misses the possibility of spontaneous emission [3]).

3. Only the dominant electric dipole interaction has been considered (which will often be a very good approximation).

4. The wavelength of the light has been assumed to be much larger than the length of the molecule (ditto).

5. The duration of the perturbation has been assumed to be long enough for the molecule to recognise the light as a periodically oscillating electric field (see the limit as $t \to \infty$ in eq. (1.47)).

6. It has been assumed that only one initial quantum state $|\psi_i\rangle$ of the molecule is populated when the light is switched on. (This will not generally be the case in an ordinary absorption experiment, which is more likely to see a thermally averaged absorption cross section

$$\sigma_T(\omega) = \frac{1}{q}\sum_i \sigma_i(\omega)\, e^{-E_i/kT} \tag{1.53}$$

where

$$q = \sum_i e^{-E_i/kT}. \tag{1.54}$$

However, modern laser experiments are capable of measuring the more fundamental initial state-resolved absorption cross section $\sigma_i(\omega)$ directly.)

In the following three lectures we shall investigate the implications of the expression for the absorption cross section in eq. (1.51) for both bound-bound electronic spectroscopy and bound-continuum molecular photodissociation.

2 Theory of Electronic Spectroscopy

Recall Fermi's Golden Rule for the absorption cross section

$$\sigma_i(\omega) = \frac{\pi\omega}{\hbar\epsilon_0 c} \sum_f \delta(\omega - \omega_{fi}) \, | \, \mathbf{M}_{fi} \cdot \mathbf{e} \, |^2 \tag{2.1}$$

where

$$\mathbf{M}_{fi} = \langle \psi_f \mid \mu \mid \psi_i \rangle \tag{2.2}$$

and $\mathbf{e}$ is a unit vector in the direction of the electric field of the light.

In this lecture we shall investigate the implications of eq. (2.1) for ordinary (bound-bound) electronic spectroscopy [5] in preparation for the extension to molecular photodissociation in lecture 3.

2.1 Rotational selection rules

The initial and final quantum states $\mid \psi_i \rangle$ and $\mid \psi_f \rangle$ in eq. (2.2) are solutions of the Schrödinger equation

$$H \, |\psi_n\rangle = E_n \, |\psi_n\rangle \tag{2.3}$$

where H is the full (electronic, vibrational and rotational) Hamiltonian of the molecule. This Hamiltonian commutes with the angular momentum operators J^2 and J_z, and we can therefore label the molecular eigenstates $|\psi_n\rangle$ with quantum numbers J and M:

$$|\psi_n\rangle \equiv |n J_n M_n\rangle \, . \tag{2.4}$$

The dipole moment operator μ in eq. (2.2) is a vector operator with three Cartesian components μ_q, $q = x, y, z$. However, it is more convenient to work with the spherical equivalent $\overline{\mu}$ of μ (which is defined by analogy with the spherical harmonics Y_{1m}) [6,7]:

$$\overline{\mu}_{+1} = -\frac{1}{\sqrt{2}} (\mu_x + i\mu_y) \tag{2.5}$$

$$\overline{\mu}_0 = \mu_z \tag{2.6}$$

$$\overline{\mu}_{-1} = +\frac{1}{\sqrt{2}} (\mu_x - i\mu_y) \, . \tag{2.7}$$

The advantage of this definition is that the components of $\overline{\mu}$ transform more conveniently under a rotation of the coordinate axes than the components of μ (due again to their analogy with spherical harmonics):

$$\overline{\mu}'_m = \sum_{k=-1}^{1} \overline{\mu}_k \, D^1_{km}(\Omega) \tag{2.8}$$

where $D^1_{km}(\Omega)$ is a Wigner rotation matrix element and $\Omega = \alpha\beta\gamma$ are the Euler angles of the rotation.

Equation (2.8) implies that the states $\overline{\mu}_m \, |iJ_iM_i\rangle$ form a basis for the direct product representation $\Gamma_1 \times \Gamma_{J_i}$ of the rotation group. Since the states $|fJ_fM_f\rangle$ form a basis for the representation Γ_{J_f}, it follows that all matrix elements of the form $\langle fJ_fM_f \,|\, \overline{\mu}_m \,|\, iJ_iM_i\rangle$ will be zero by symmetry unless the direct product $\Gamma_{J_f} \times \Gamma_1 \times \Gamma_{J_i}$ contains the totally symmetric representation Γ_0. Evaluating this direct product by repeated application of the reduction formula [7]

$$\Gamma_{J'} \times \Gamma_J = \Gamma_{J'+J} + \Gamma_{J'+J-1} + \cdots + \Gamma_{|J'-J|} \tag{2.9}$$

shows that $\Gamma_{J_f} \times \Gamma_1 \times \Gamma_{J_i}$ will only contain Γ_0 if either (a) $J_i \geq 1$ and $J_f = J_i$ or $J_i \pm 1$, or (b) $J_i = 0$ and $J_f = 1$. We thus obtain the general rotational selection rule for an electric dipole transition:

$$\Delta J = 0, \pm 1 \qquad (J = 0 \not\leftrightarrow J = 0). \tag{2.10}$$

The corresponding selection rules on the projection quantum number M can be obtained by applying the Wigner-Eckart theorem [6,7] to the matrix elements of the spherical tensor operator $\overline{\mu}$:

$$\langle fJ_fM_f \,|\, \overline{\mu}_m \,|\, iJ_iM_i\rangle = \langle J_fM_f \,|\, J_i1M_im\rangle \, \langle fJ_f \,||\, \overline{\mu} \,||\, iJ_i\rangle \tag{2.11}$$

where

$$\langle fJ_f \,||\, \overline{\mu} \,||\, iJ_i\rangle = \sum_{M_im} \langle J_fM_f \,|\, J_i1M_im\rangle \, \langle fJ_fM_f \,|\, \overline{\mu}_m \,|\, iJ_iM_i\rangle \, . \tag{2.12}$$

The physical content of this theorem is that the matrix element in eq. (2.11) is the product of two factors, the first of which is a vector coupling coefficient $\langle J_fM_f \,|\, J_i1M_im\rangle$ which embodies the rotational symmetry of the problem

and the second of which is a reduced matrix element $\langle fJ_f \,||\, \overline{\mu} \,||\, iJ_i \rangle$ which contains the dynamics [6,7].

Consider (for example) the case where the electric field vector $\mathbf{e}$ of the light is parallel to the laboratory z axis (as in lecture 1). The relevant dipole matrix element is then

$$\langle fJ_fM_f \mid \mu_z \mid iJ_iM_i \rangle = \langle J_fM_f \mid J_i1M_i0 \rangle \, \langle fJ_f \,||\, \overline{\mu} \,||\, iJ_i \rangle \tag{2.13}$$

which leads (via a consideration of the properties of the vector coupling coefficient $\langle J_fM_f \mid J_i1M_i0 \rangle$) to both the selection rule on J in eq. (2.10) and the following selection rule on M:

$$\Delta M = 0. \tag{2.14}$$

The selection rules on M for other polarisations can also be obtained from eq. (2.11) with the help of eqs. (2.5) to (2.7).

(The selection rule on J in eq. (2.10) is often attributed to the conservation of angular momentum, with a photon of light contributing one unit of angular momentum to the molecule. This is also clearly a very natural interpretation of the vector coupling coefficient $\langle J_fM_f \mid J_i1M_i0 \rangle$ in eq. (2.13). However, note again that the classical electromagnetic wave we have used to derive eq. (2.10) is not quantised and does not contain any reference to h.)

2.2 The Born-Oppenheimer approximation

We cannot now go any further without actually solving the Schrödinger equation in eq. (2.3). The standard way to do this is to exploit the different time scales of electronic and nuclear motion by writing the Hamiltonian $H(\mathbf{r},\mathbf{R})$ as

$$H(\mathbf{r},\mathbf{R}) = T^n(\mathbf{R}) + H^e(\mathbf{r},\mathbf{R}) \tag{2.15}$$

where $T^n(\mathbf{R})$ is the nuclear kinetic energy operator and $H^e(\mathbf{r},\mathbf{R})$ is the electronic Hamiltonian (containing the electronic kinetic energy and electronic and nuclear potential energy operators) at each value of the nuclear coordinates $\mathbf{R}$.

The wavefunction $|\psi(\mathbf{r},\mathbf{R})\rangle$ in eq. (2.3) can then be expanded as

$$|\psi(\mathbf{r},\mathbf{R})\rangle = \sum_k |\psi_k^e(\mathbf{r};\mathbf{R})\, \psi_k^n(\mathbf{R})\rangle \tag{2.16}$$

where $|\psi_k^e(\mathbf{r};\mathbf{R})\rangle$ satisfies the electronic Schrödinger equation

$$H^e(\mathbf{r},\mathbf{R})\,|\psi_k^e(\mathbf{r};\mathbf{R})\rangle = V_k^e(\mathbf{R})\,|\psi_k^e(\mathbf{r};\mathbf{R})\rangle \tag{2.17}$$

subject to

$$\langle\psi_j^e(\mathbf{r};\mathbf{R})\,|\,\psi_k^e(\mathbf{r};\mathbf{R})\rangle_{\mathbf{r}} \equiv \int \psi_j^e(\mathbf{r};\mathbf{R})^*\psi_k^e(\mathbf{r};\mathbf{R})\,d\mathbf{r} = \delta_{jk} \tag{2.18}$$

and the eigenvalue $V_k^e(\mathbf{R})$ in eq. (2.17) is an adiabatic electronic potential energy surface.

Substituting eq. (2.16) into eq. (2.3) and making use of the orthonormality condition in eq. (2.18) gives a system of coupled equations for the nuclear wavefunctions

$$\sum_k \langle\psi_j^e(\mathbf{r};\mathbf{R})|\,T^n(\mathbf{R})\,|\psi_k^e(\mathbf{r};\mathbf{R})\,\psi_k^n(\mathbf{R})\rangle_{\mathbf{r}} + [\,V_j^e(\mathbf{R}) - E\,]|\psi_j^n(\mathbf{R})\rangle = 0. \tag{2.19}$$

These coupled equations are still exact, but they are generally very difficult to solve exactly (not least because of the derivatives of excited electronic wavefunctions with respect to nuclear coordinates that are implied by the above matrix elements of $T^n(\mathbf{R})$). The usual way out of this difficulty is to assume that the electronic wavefunctions vary more slowly than the nuclear wavefunctions as a function of the nuclear coordinates. The derivatives of the electronic wavefunctions can then be neglected to leave the Born-Oppenheimer (adiabatic) approximation

$$|\psi(\mathbf{r},\mathbf{R})\rangle \simeq |\psi_j^e(\mathbf{r};\mathbf{R})\,\psi_j^n(\mathbf{R})\rangle \tag{2.20}$$

where

$$H_j^n(\mathbf{R})|\psi_j^n(\mathbf{R})\rangle = E\,|\psi_j^n(\mathbf{R})\rangle \tag{2.21}$$

with

$$H_j^n(\mathbf{R}) = T^n(\mathbf{R}) + V_j^e(\mathbf{R}). \tag{2.22}$$

This approximation will be reliable if the j-th electronic potential energy surface is well separated from the other electronic potential energy surfaces of the same symmetry in the region of nuclear coordinate space of interest. This is often the case for the ground electronic potential energy surface of each symmetry, but it can easily break down for the excited surfaces that are accessed in electronic spectroscopy and molecular photodissociation. If

it does break down, one has to return to a more accurate treatment based on eq. (2.19), and a discussion of how to do this is given in Schinke's book [1]. For the purposes of the present course we shall simply assume that the Born-Oppenheimer approximation in eq. (2.20) is sufficiently accurate for both the initial and final quantum states $|\psi_i\rangle$ and $|\psi_f\rangle$ in eq. (2.2).

2.3 Electronic selection rules

Now consider what happens when the Born-Oppenheimer approximation is substituted into the expression for the dipole matrix element in eq. (2.2):

$$\mathbf{M}_{fi} = \langle \psi_f^e(\mathbf{r};\mathbf{R})\, \psi_f^n(\mathbf{R}) \,|\, \mu(\mathbf{r},\mathbf{R}) \,|\, \psi_i^e(\mathbf{r};\mathbf{R})\, \psi_i^n(\mathbf{R}) \rangle \tag{2.23}$$

where

$$\mu(\mathbf{r},\mathbf{R}) = \mu^e(\mathbf{r}) + \mu^n(\mathbf{R}). \tag{2.24}$$

Two distinct cases arise, depending on whether or not the initial and final electronic wavefunctions $|\psi_i^e(\mathbf{r};\mathbf{R})\rangle$ and $|\psi_f^e(\mathbf{r};\mathbf{R})\rangle$ are the same.

If $|\psi_i^e(\mathbf{r};\mathbf{R})\rangle$ and $|\psi_f^e(\mathbf{r};\mathbf{R})\rangle$ are the same, as in vibrational-rotational or pure rotational spectroscopy, we can use the fact that $|\psi_i^e(\mathbf{r};\mathbf{R})\rangle$ is normalised to write eq. (2.23) as

$$\mathbf{M}_{fi} = \langle \psi_f^n(\mathbf{R}) \,|\, \mu_i(\mathbf{R}) \,|\, \psi_i^n(\mathbf{R}) \rangle_{\mathbf{R}} \tag{2.25}$$

where

$$\mu_i(\mathbf{R}) = \langle \psi_i^e(\mathbf{r};\mathbf{R}) \,|\, \mu^e(\mathbf{r}) \,|\, \psi_i^e(\mathbf{r};\mathbf{R}) \rangle_{\mathbf{r}} + \mu^n(\mathbf{R}) \tag{2.26}$$

is the dipole moment of the molecule in the electronic state $|\psi_i^e(\mathbf{r};\mathbf{R})\rangle$. We thus obtain the gross selection rules for vibrational-rotational and pure rotational spectroscopy, namely that the molecule must have a permanent dipole moment $\mu_i(\mathbf{R}) \neq 0$ at its equilibrium geometry in order to exhibit a microwave absorption spectrum and a permanent dipole moment gradient $\nabla_{\mathbf{R}}\mu_i(\mathbf{R}) \neq 0$ in order to exhibit an IR spectrum (so that the matrix element $\mathbf{M}_{fi}$ in eq. (2.25) does not vanish by virtue of the orthogonality of the initial and final vibrational wavefunctions).

If on the other hand $|\psi_f^e(\mathbf{r};\mathbf{R})\rangle$ and $|\psi_i^e(\mathbf{r};\mathbf{R})\rangle$ are different, as in electronic spectroscopy, we can use the fact that they are orthogonal to write eq. (2.23) as

$$\mathbf{M}_{fi} = \langle \psi_f^n(\mathbf{R}) \,|\, \mu_{fi}(\mathbf{R}) \,|\, \psi_i^n(\mathbf{R}) \rangle_{\mathbf{R}} \tag{2.27}$$

where

$$\mu_{fi}(\mathbf{R}) = \langle \psi_f^e(\mathbf{r};\mathbf{R}) \,|\, \mu^e(\mathbf{r}) \,|\, \psi_i^e(\mathbf{r};\mathbf{R}) \rangle_{\mathbf{r}} \tag{2.28}$$

is the electric dipole transition matrix element for the electronic transition. This transition matrix element is the origin of electronic selection rules.

Consider (for example) the case of a heteronuclear diatomic molecule. The dipole moment operator $\mu^e(\mathbf{r})$ will have one component parallel to the internuclear axis (Σ^+) and two degenerate components perpendicular to the axis (Π), and the initial and final electronic wavefunctions $|\psi_i^e(\mathbf{r};\mathbf{R})\rangle$ and $|\psi_f^e(\mathbf{r};\mathbf{R})\rangle$ will be bases for irreducible representations Γ_i^e and Γ_f^e of $C_{\infty v}$. A parallel electronic transition will therefore be forbidden (i.e., $\mu_{fi}(\mathbf{R})$ will be zero) unless the direct product $\Gamma_f^e \times \Sigma^+ \times \Gamma_i^e = \Gamma_f^e \times \Gamma_i^e$ contains the totally symmetric representation Σ^+. This implies that $\Gamma_f^e = \Gamma_i^e$, which gives the electronic selection rule

$$\Delta\Lambda = 0 \qquad (\mu_{fi} \parallel \mathbf{R}) \tag{2.29}$$

for a parallel electronic transition in a heteronuclear diatomic. The corresponding selection rule for a perpendicular transition

$$\Delta\Lambda = \pm 1 \qquad (\mu_{fi} \perp \mathbf{R}) \tag{2.30}$$

follows similarly from the direct product $\Gamma_f^e \times \Pi \times \Gamma_i^e$, and electronic selection rules for other molecules are obtained in the same way.

2.4 Vibrational Franck-Condon factors

Having now dealt with electronic selection rules we can dispense with the electronic part of the problem and assume that $\mu_{fi}(\mathbf{R})$, $V_f^e(\mathbf{R})$ and $V_i^e(\mathbf{R})$ are known. We can also dispense with the ns in eq. (2.27), because everything from this point on will be confined to the nuclear motion.

With this accepted, eq. (2.27) becomes

$$\mathbf{M}_{fi}\cdot\mathbf{e} = \langle \psi_f(\mathbf{R}) \,|\, \mu_{fi}\cdot\mathbf{e} \,|\, \psi_i(\mathbf{R}) \rangle_{\mathbf{R}} \tag{2.31}$$

where $|\psi_i(\mathbf{R})\rangle$ and $|\psi_f(\mathbf{R})\rangle$ are the initial and final *ro-vibrational* wavefunctions of the molecule and $\mu_{fi}(\mathbf{R})$ is the dipole matrix element for the electronic transition.

It is instructive to consider eq. (2.31) in more detail for the special case of a ${}^1\Sigma \leftrightarrow {}^1\Sigma$ electronic transition in a diatomic molecule. This case is uniquely simple because the initial and final ro-vibrational wavefunctions can each be written exactly as the product of a vibrational and a rotational function:

$$|\psi_i(\mathbf{R})\rangle = |\psi_{v_i J_i}(R)\, Y_{J_i M_i}(\hat{\mathbf{R}})\rangle \tag{2.32}$$

$$|\psi_f(\mathbf{R})\rangle = |\psi_{v_f J_f}(R)\, Y_{J_f M_f}(\hat{\mathbf{R}})\rangle. \tag{2.33}$$

Furthermore, since $\Delta\Lambda = 0$ for a $\Sigma \leftrightarrow \Sigma$ transition, we know from eq. (2.29) that the dipole transition matrix element $\mu_{fi}(\mathbf{R})$ will be parallel to $\mathbf{R}$:

$$\mu_{fi}(\mathbf{R})\cdot\mathbf{e} = \mu_{fi}(R)\,\hat{\mathbf{R}}\cdot\mathbf{e} \tag{2.34}$$

(where $\mu_{fi}(R)$ is the length of the vector $\mu_{fi}(\mathbf{R})$). The matrix element in eq. (2.31) therefore factors exactly into a product of vibrational and rotational matrix elements

$$\begin{aligned}\mathbf{M}_{fi}\cdot\mathbf{e} = {} & \langle \psi_{v_f J_f}(R)\,|\,\mu_{fi}(R)\,|\,\psi_{v_i J_i}(R)\rangle_R \\ & \times \langle Y_{J_f M_f}(\hat{\mathbf{R}})\,|\,\hat{\mathbf{R}}\cdot\mathbf{e}\,|\,Y_{J_i M_i}(\hat{\mathbf{R}})\rangle_{\hat{\mathbf{R}}}\end{aligned} \tag{2.35}$$

the first of which contains the vibrational dynamics of the transition and the second of which is responsible for rotational selection rules.

When the electric field vector of the light is parallel to the laboratory z axis, so that $\hat{\mathbf{R}}\cdot\mathbf{e} = \cos\theta$, the rotational matrix element in eq. (2.35) can be worked out analytically and leads to the specific rotational selection rules $\Delta J = \pm 1$ and $\Delta M = 0$. If these selection rules are satisfied, the matrix element is just a number

$$f_{J_f J_i M_i} = \langle Y_{J_f M_f}(\hat{\mathbf{R}})\,|\,\hat{\mathbf{R}}\cdot\mathbf{e}\,|\,Y_{J_i M_i}(\hat{\mathbf{R}})\rangle_{\hat{\mathbf{R}}} \tag{2.36}$$

and since this number is the same for all vibrational bands v_f it need not concern us any further.

The interesting part of eq. (2.35) is the vibrational matrix element. This can be simplified by noting that the vibrational wavefunctions $|\psi_{v_i J_i}(R)\rangle$ and $|\psi_{v_f J_f}(R)\rangle$ will often depend only weakly on the rotational quantum numbers J_i and J_f, especially for low rotational quantum numbers, and that the electronic dipole matrix element $\mu_{fi}(R)$ will often be a slowly varying function of R in the region $R \simeq R_e$ where $|\psi_{v_i J_i}(R)\rangle$ is significant.

We can therefore make the Condon approximations [10]

$$|\psi_{v_i J_i}(R)\rangle \simeq |\psi_{v_i 0}(R)\rangle \tag{2.37}$$

$$|\psi_{v_f J_f}(R)\rangle \simeq |\psi_{v_f 0}(R)\rangle \tag{2.38}$$

$$\mu_{fi}(R) \simeq \mu_{fi}(R_e) \tag{2.39}$$

which reduce eq. (2.35) to

$$\mathbf{M}_{fi}\cdot\mathbf{e} \simeq \mu_{fi}(R_e)\,\langle\psi_{v_f 0}\,|\,\psi_{v_i 0}\rangle\, f_{J_f J_i M_i} \tag{2.40}$$

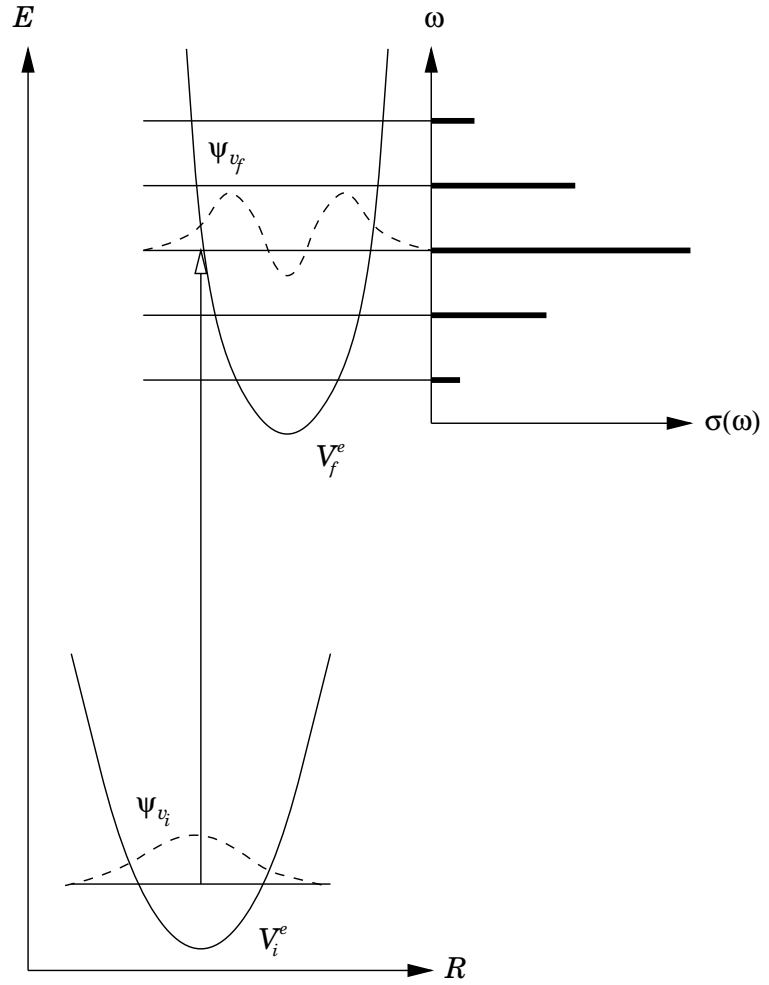
and hence

$$|\,\mathbf{M}_{fi}\cdot\mathbf{e}\,|^2 \simeq |\mu_{fi}(R_e)|^2\,|\langle\psi_{v_f 0}\,|\,\psi_{v_i 0}\rangle|^2\,|f_{J_f J_i M_i}|^2. \tag{2.41}$$

The intensity of the transition from the initial state i to the final state f is thus proportional to three factors, one electronic, one vibrational, and one rotational. Of these, only the vibrational Franck-Condon factor $|\langle\psi_{v_f 0}\,|\,\psi_{v_i 0}\rangle|^2$ depends on the final vibrational quantum number v_f, and this factor is therefore responsible for the different intensities of different vibrational bands. We thus obtain the standard picture of electronic spectroscopy shown on the next page, in which the Franck-Condon principle and the Correspondence principle combine to explain the observed vibrational structure in an electronic absorption spectrum [10]. A similar result can also be derived for polyatomic molecules by considering an adiabatic separation of vibrations and rotations.

2.5 Summary

This completes our discussion of the information that can be extracted from the expression for the absorption cross section in eq. (2.1). Much of this information applies equally well to molecular photodissociation as it does to electronic spectroscopy, including in particular everything we have said about the Born-Oppenheimer approximation and selection rules. Nevertheless, eq. (2.1) cannot be used directly to describe photodissociation, because it involves a sum over a discrete set of final molecular quantum states. We shall return to eliminate this problem in lecture 3.


E
ω
ψ_{v_f}
V_f^e
σ(ω)
ψ_{v_i}
V_i^e
R

3 Theory of Molecular Photodissociation

Recall that the absorption cross section for a bound-bound electronic transition can be written within the Born-Oppenheimer approximation as

$$\sigma_i(\omega) = \frac{\pi\omega}{\hbar\epsilon_0 c} \sum_f \delta(\omega - \omega_{fi}) \left| \langle \psi_f \,|\, \mu_{fi}\cdot\mathbf{e} \,|\psi_i\rangle \right|^2 \tag{3.1}$$

where $|\psi_i\rangle$ and $|\psi_f\rangle$ are the initial and final ro-vibrational wavefunctions of the molecule and μ_{fi} is the electric dipole transition matrix element for the electronic transition.

We shall begin this lecture by rearranging eq. (3.1) into a form that does not involve an explicit sum over a discrete set of final quantum states and therefore applies equally well to both bound-bound electronic spectroscopy and bound-continuum molecular photodissociation.

3.1 The absorption spectrum

The first change that is needed to get eq. (3.1) into a more useful form is to replace the delta function in ω with a delta function in E:

$$\delta(\omega - \omega_{fi}) = \hbar\, \delta(E - E_{fi}) \tag{3.2}$$

where $E = \hbar\omega$ and $E_{fi} = E_f - E_i$. In particular, if we choose the zero of the energy scale to be the energy of the initial quantum state E_i, eq. (3.1) becomes

$$\sigma_i(\omega) = \frac{\pi\omega}{\epsilon_0 c}\, P_i(E) \tag{3.3}$$

where

$$P_i(E) = \sum_f \langle \chi_i \,|\, \psi_f \rangle\, \delta(E - E_f)\, \langle \psi_f \,|\, \chi_i \rangle\,. \tag{3.4}$$

with

$$|\chi_i\rangle = \mu_{fi}\cdot\mathbf{e}\,|\psi_i\rangle. \tag{3.5}$$

The absorption cross section $\sigma_i(\omega)$ is thus proportional to ω times an absorption spectrum $P_i(E)$, and we shall concentrate on $P_i(E)$ from this point on to save having to carry the constant of proportionality.

The aim is now to eliminate the sum over f from the expression for $P_i(E)$ in eq. (3.4), and this can be achieved as follows. The final ro-vibrational wavefunction $|\psi_f\rangle$ satisfies the time-independent Schrödinger equation

$$H\,|\psi_f\rangle = E_f\,|\psi_f\rangle \tag{3.6}$$

subject to the usual conditions

$$\langle \psi_{f'} \mid \psi_f \rangle = \delta_{f'f} \tag{3.7}$$

and

$$\sum_f |\psi_f\rangle \langle \psi_f| = 1 \tag{3.8}$$

where H is the Hamiltonian of the molecule on the final Born-Oppenheimer electronic potential energy surface V_f^e.

Now it is easy to show by induction that eq. (3.6) implies

$$H^n|\psi_f\rangle = E_f^n|\psi_f\rangle \tag{3.9}$$

for any integer $n \geq 0$, and therefore that

$$p(H)|\psi_f\rangle = p(E_f)|\psi_f\rangle \tag{3.10}$$

for any polynomial function $p(H)$ (and more generally for any function with a convergent power series expansion). This equation can be inverted by multiplying both sides by the operator $p(H)^{-1}p(E_f)^{-1}$ to give

$$p(H)^{-1}|\psi_f\rangle = p(E_f)^{-1}|\psi_f\rangle \tag{3.11}$$

and this in turn can be combined with eq. (3.10) to give

$$p(H)^{-1}q(H)|\psi_f\rangle = p(E_f)^{-1}q(E_f)|\psi_f\rangle \tag{3.12}$$

where $p(H)$ and $q(H)$ are arbitrary polynomial functions of H. Hence the general eigenvalue equation

$$f(H)|\psi_f\rangle = f(E_f)|\psi_f\rangle \tag{3.13}$$

and the corresponding spectral representation

$$f(H) = f(H)\sum_f |\psi_f\rangle\langle\psi_f| = \sum_f |\psi_f\rangle f(E_f)\langle\psi_f| \tag{3.14}$$

are both guaranteed to hold for a large class of "sensible" functions $f(H)$ (including all rational functions of the form $p(H)^{-1}q(H)$ where $p(H)$ and $q(H)$ are either polynomials or transcendental functions like $\sin(H)$ and $\cos(H)$ with convergent power series expansions).

Equation (3.14) is clearly very similar to eq. (3.4), except that the delta function $\delta(E - E_f)$ in eq. (3.4) is not a proper function and cannot be classified as "sensible". The solution to this difficulty is simply to write the delta function as the limit of a pre-limit delta function $\delta_\epsilon(E - H)$ which can be used in eq. (3.14). (This is, after all, where the delta function came from in the first place – see eq. (1.47) in lecture 1.) Thus

$$P_i(E) = \lim_{\epsilon \to 0} \sum_f \langle \chi_i \,|\, \psi_f \rangle \, \delta_\epsilon(E - E_f) \, \langle \psi_f \,|\, \chi_i \rangle \tag{3.15}$$

can be written as

$$P_i(E) = \lim_{\epsilon \to 0} \langle \chi_i \,|\, \delta_\epsilon(E - H) \,|\, \chi_i \rangle \tag{3.16}$$

where (for example)

$$\delta_\epsilon(E - H) = \left(\frac{1}{\pi\epsilon}\right)^{1/2} e^{-(E-H)^2/\epsilon} = \left(\frac{1}{\pi\epsilon}\right)^{1/2} \sum_{n=0}^{\infty} \frac{[-(E - H)^2/\epsilon]^n}{n!} \tag{3.17}$$

is a sensible function with a convergent power series expansion.

Equation (3.16) for the absorption spectrum $P_i(E)$ is the single most important result in this lecture. Since it does not contain any reference to a discrete set of final quantum states it applies equally well to both bound-bound electronic spectroscopy and bound-continuum molecular photodissociation. Furthermore, as we shall see below, it leads directly to all of the usual time-dependent and time-independent methods for calculating photodissociation cross sections simply by choosing different expressions for the pre-limit delta function $\delta_\epsilon(E - H)$.

3.2 Time-dependent theory

One of the most familiar representations of the delta function is the Fourier representation

$$\delta(E - H) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{+i(E-H)t/\hbar} \, dt \tag{3.18}$$

which we have already used at least once (albeit in a slightly different form) in section 1.3. The limit as $\epsilon \to 0$ has already been taken in eq. (3.18); two possible pre-limit versions are

$$\delta_\epsilon(E - H) = \frac{1}{\pi\hbar} \mathrm{Re} \int_0^{\infty} e^{+i(E+i\epsilon-H)t/\hbar} \, dt$$

$$= \frac{1}{\pi}\mathrm{Re}\left[\frac{i}{E+i\epsilon-H}\right]$$
$$= \frac{1}{\pi}\frac{\epsilon}{(E-H)^2+\epsilon^2} \tag{3.19}$$

and

$$\delta_\epsilon(E-H) = \frac{1}{\pi\hbar}\mathrm{Re}\int_{-\infty}^{0} e^{+i(E-i\epsilon-H)t/\hbar}\,dt$$
$$= \frac{1}{\pi}\mathrm{Re}\left[\frac{-i}{E-i\epsilon-H}\right]$$
$$= \frac{1}{\pi}\frac{\epsilon}{(E-H)^2+\epsilon^2} \tag{3.20}$$

both of which are rational functions of H and can therefore be used in eq. (3.14).

It is slightly more natural to use the delta function in eq. (3.19), which involves an integral over positive t. When this is substituted into eq. (3.16) we obtain the absorption spectrum $P_i(E)$ as the (half) Fourier transform of an autocorrelation function $C_i(t)$ [11]

$$P_i(E) = \lim_{\epsilon\to 0}\frac{1}{\pi\hbar}\mathrm{Re}\int_0^\infty e^{+iEt/\hbar}C_i(t)\,dt \tag{3.21}$$

where

$$C_i(t) = \langle\chi_i \mid e^{-i(H-i\epsilon)t/\hbar}\mid\chi_i\rangle\,. \tag{3.22}$$

Notice in particular that the integral over t in eq. (3.21) is guaranteed to converge by virtue of the factor $e^{-\epsilon t/\hbar}$ in eq. (3.22). This factor *must* therefore be included (in general) when doing the calculation and the limit as $\epsilon\to 0$ taken at the end.

Equations (3.21) and (3.22) have a very appealing physical interpretation. The initial ro-vibrational wavefunction $|\psi_i\rangle$ of the molecule is first projected onto the final electronic potential energy surface to give an initial wavepacket $|\chi_i(0)\rangle = \mu_{fi}\cdot\mathbf{e}\,|\psi_i\rangle$ at time $t=0$. This wavepacket then evolves in time on the excited surface as a solution of the time-dependent Schrödinger equation

$$|\chi_i(t)\rangle = e^{-i(H-i\epsilon)t/\hbar}\,|\chi_i(0)\rangle \tag{3.23}$$

and the overlap of the wavepacket at time t with the wavepacket at time 0 gives the autocorrelation function

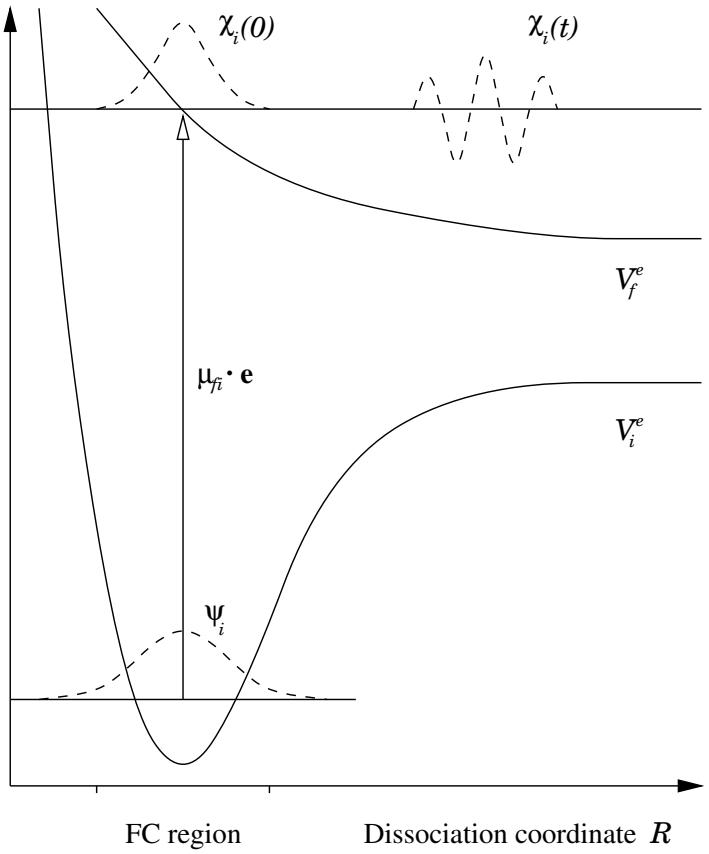
$$C_i(t) = \langle\chi_i(0)\mid\chi_i(t)\rangle\,. \tag{3.24}$$

Finally, the absorption spectrum (or power spectrum) $P_i(E)$ corresponding to this autocorrelation function is given by the time-to-energy Fourier transform in eq. (3.21).

The advantage of this picture is that it allows one to unravel the dynamics of the photodissociation either by studying the behaviour of $P_i(E)$ *or* by studying the behaviour of $C_i(t)$, whichever happens to be the most convenient. We shall illustrate this advantage in the next section by considering the contrasting cases of direct photodissociation and bound-bound electronic spectroscopy.

3.3 Resonances and recurrences

Consider first the case of direct photodissociation shown below, where the wavepacket simply departs the Franck-Condon region and dissociates:



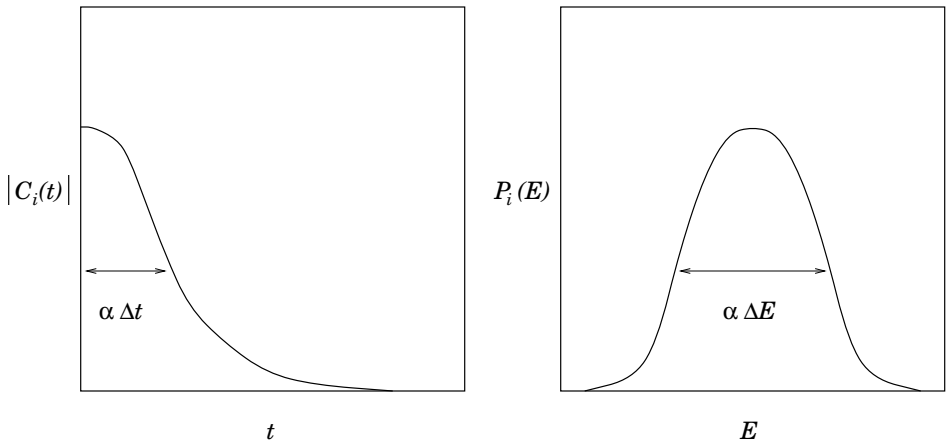
It follows from eq. (3.24) that the autocorrelation function $C_i(t)$ will decay smoothly in this situation from its initial value $C_i(0) = \langle \chi_i \mid \chi_i \rangle$ to zero. This behaviour can be modelled (for example) by the complex Gaussian function

$$C_i(t) = \langle \chi_i \mid \chi_i \rangle \; e^{-t^2/(2\Delta t^2) - iE_0 t/\hbar} \tag{3.25}$$

which involves two parameters Δt and E_0 (corresponding respectively to the characteristic time scale of the decay and the mean energy contained in the initial wavepacket). This model for $C_i(t)$ is straightforward to Fourier transform and leads to the following expression for the absorption spectrum $P_i(E)$:

$$P_i(E) = \frac{1}{\sqrt{2\pi\Delta E^2}} \langle \chi_i \mid \chi_i \rangle \; e^{-(E-E_0)^2/2\Delta E^2} \tag{3.26}$$

where $\Delta E = \hbar/\Delta t$. The absorption spectrum for direct photodissociation will thus simply be a broad featureless curve centred on the mean energy E_0 with a width that reflects the time taken for the wavepacket to leave the Franck-Condon region (and therefore, from Ehrenfest's theorem, the slope of the final electronic potential energy surface V_f^e in the Franck-Condon region):



Direct Photodissociation

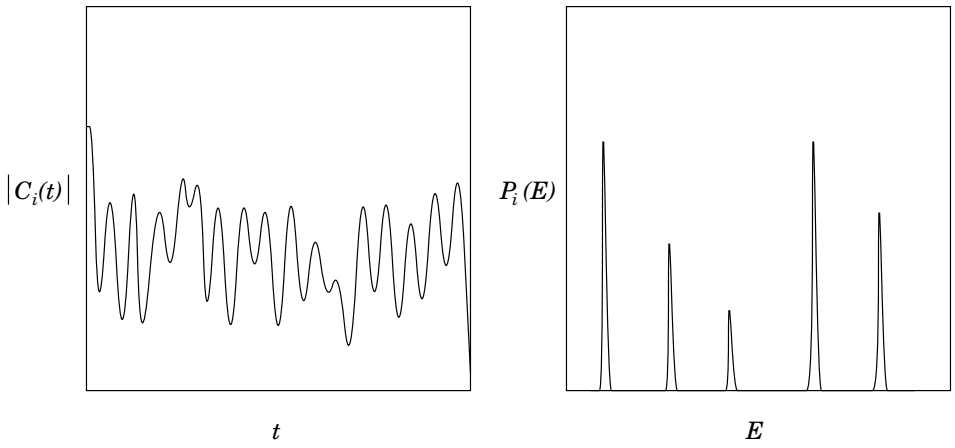
At the other extreme, consider the case of bound-bound electronic spectroscopy (an appropriate diagram for which was given at the end of lecture 2). The absorption spectrum for this case is given by eq. (3.4) as a series of sharp lines weighted by Franck-Condon factors $|\langle \chi_i \,|\, \psi_f \rangle|^2$:

$$P_i(E) = \sum_f |\langle \chi_i \,|\, \psi_f \rangle|^2 \; \delta(E - E_f). \tag{3.27}$$

The inverse Fourier transform of this equation gives the autocorrelation function $C_i(t)$ as

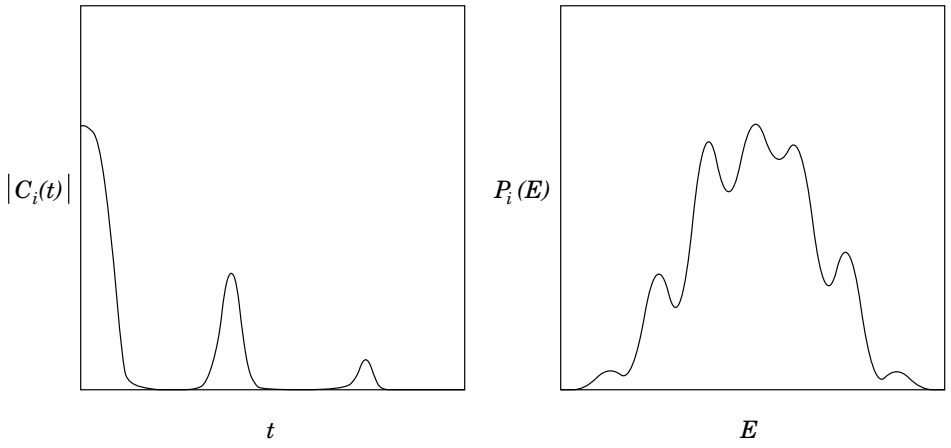
$$C_i(t) = \int_{-\infty}^{\infty} e^{-iEt/\hbar} P_i(E)\, dE = \sum_f |\langle \chi_i \,|\, \psi_f \rangle|^2 \; e^{-i\omega_f t} \tag{3.28}$$

where $\omega_f = E_f/\hbar$ is the angular frequency associated with the final rovibronic energy level E_f. It follows that $|C_i(t)|$ will remain of the same order of magnitude as its initial value $|\langle \chi_i \,|\, \chi_i \rangle|$ for all time and exhibit a complicated pattern of oscillations that reflects the interference between the different terms in eq. (3.28), in complete contrast to its behaviour in the case of direct photodissociation considered above:



Electronic Spectroscopy

It should now be easy to visualise the behaviour of both $C_i(t)$ and $P_i(E)$ for the case of indirect photodissociation, which lies between the direct photodissociation and electronic spectroscopy extremes. Here most of the initial wavepacket leaves the Franck-Condon region never to return, but at least some fraction returns at regular intervals giving rise to recurrences in $C_i(t)$. The resulting absorption spectrum depends on the strength of the recurrences. If the recurrences are strong, the situation will be closer to the electronic spectroscopy extreme and the absorption spectrum will be dominated by narrow resonances. However, if the recurrences are weak, the situation will be closer to the direct photodissocation extreme and the absorption spectrum will consist of a broad envelope modulated by diffuse vibrational structure as shown in the diagram below. We shall give some examples of how both types of behaviour can be found in real systems at the end of lecture 4.



Indirect Photodissociation

3.4 Time-independent theory

An entirely equivalent time-independent theory for the absorption spectrum follows from the expression for the pre-limit delta function in the second line of eq. (3.20):

$$\delta_\epsilon(E - H) = \frac{1}{\pi}\mathrm{Im}\, G^-(E) \tag{3.29}$$

where

$$G^-(E) = \frac{i}{\hbar}\int_{-\infty}^{0} e^{+i(E-i\epsilon-H)t/\hbar}\, dt = (E - i\epsilon - H)^{-1} \tag{3.30}$$

is the incoming-wave scattering Green's function (see Miller's lecture notes). In particular, substituting eq. (3.29) into eq. (3.16) gives

$$P_i(E) = \lim_{\epsilon\to 0}\frac{1}{\pi}\mathrm{Im}\langle\chi_i\,|\,G^-(E)\,|\,\chi_i\rangle \tag{3.31}$$

which shows that the absorption spectrum can be calculated at each required energy as a diagonal matrix element of the Green's function. (Note also that the limit as $\epsilon \to 0$ must again be taken at the end of the calculation, because the Green's function in eq. (3.30) is not properly defined in the limit as $\epsilon \to 0$ when E is in the continuous spectrum of H [8].)

Although eq. (3.31) is equivalent to eq. (3.21), it is not generally so useful from the point of view of understanding the photodissociation dynamics so we shall not discuss it any further.

3.5 Partial cross sections

Everything we have said up to this point has been confined to the calculation of the total absorption spectrum from a given initial state $P_i(E)$, and hence from eq. (3.3) the corresponding total absorption cross section $\sigma_i(\omega)$. However, it is equally important to be able to calculate the partial absorption cross section $\sigma_{fi}(\omega)$ into each final quantum state f of the photofragments in order to simulate experiments with product quantum state resolution. This partial absorption cross section is proportional to ω times a partial absorption spectrum $P_{fi}(E)$

$$\sigma_{fi}(\omega) = \frac{\pi\omega}{\epsilon_0 c}P_{fi}(E) \tag{3.32}$$

and we shall work again with $P_{fi}(E)$ rather than $\sigma_{fi}(\omega)$ to save having to carry the constant of proportionality.

Although we have avoided them up to this point, it is difficult to develop a theory for $P_{fi}(E)$ without introducing continuum wavefunctions. We shall therefore begin with the continuum analogues of eqs. (3.6) to (3.8):

$$H \,|\, \psi_f^-(E)\rangle = E \,|\, \psi_f^-(E)\rangle \tag{3.33}$$

where

$$\langle \psi_{f'}^-(E') \,|\, \psi_f^-(E)\rangle = \delta_{f'f}\delta(E' - E) \tag{3.34}$$

and

$$\sum_f \int |\psi_f^-(E)\rangle\langle\psi_f^-(E)|\, dE = 1. \tag{3.35}$$

These equations have been written assuming that $|\psi_f^-(E)\rangle$ is energy-normalised (as in eq. (3.34)), and it should be emphasised again that the sum over f in eq. (3.35) is a sum over *photofragment* quantum states rather than a sum over molecular bound states as in eq. (3.8). Note also that the minus sign in $|\psi_f^-(E)\rangle$ refers to the scattering boundary conditions, which have been chosen here to correspond to incoming waves in all open photofragment channels plus a scattered outgoing wave in channel f.

Equations (3.33) and (3.35) can be combined using an argument identical to the one in section 3.1 to show that the continuum version of the spectral representation

$$f(H) = \sum_f \int |\psi_f^-(E)\rangle f(E) \langle\psi_f^-(E)|\, dE \tag{3.36}$$

holds for the same class of functions $f(H)$ as the discrete version in eq. (3.14). It therefore holds for a pre-limit delta function of the form in eq. (3.17) (or eq. (3.19) or eq. (3.20)):

$$\delta_\epsilon(E - H) = \sum_f \int |\psi_f^-(E')\rangle \delta_\epsilon(E - E') \langle\psi_f^-(E')|\, dE'. \tag{3.37}$$

Furthermore, in contrast to the situation in eqs. (3.21) and (3.31), where it was essential not to take the limit as $\epsilon \to 0$ until the end of the calculation,

the right-hand side of eq. (3.37) can be taken to the limit without any difficulty because of the integral over E':

$$\begin{aligned}\delta(E-H) &= \lim_{\epsilon\to 0}\delta_\epsilon(E-H)\\ &= \sum_f \int |\psi_f^-(E')\rangle\delta(E-E')\langle\psi_f^-(E')|\,dE'\\ &= \sum_f |\psi_f^-(E)\rangle\langle\psi_f^-(E)|. \end{aligned} \tag{3.38}$$

Substituting eq. (3.38) into eq. (3.16) immediately gives the total absorption spectrum $P_i(E)$ as a sum of partial absorption spectra $P_{fi}(E)$ into each final photofragment state:

$$P_i(E) = \sum_f P_{fi}(E) \tag{3.39}$$

where

$$P_{fi}(E) = |\langle\psi_f^-(E)\,|\,\chi_i\rangle|^2. \tag{3.40}$$

However, we still have to solve the Schrödinger equation in eq. (3.33) subject to appropriate scattering boundary conditions to obtain the scattering wavefunction $|\psi_f^-(E)\rangle$.

The standard way to do this is to use the Lippmann-Schwinger equation [8], which rolls the Schrödinger equation and the scattering boundary conditions into one (see also Miller's lecture notes on scattering theory):

$$|\psi_f^-(E)\rangle = |\phi_f(E)\rangle + \lim_{\epsilon\to 0} G^-(E)V_f\,|\phi_f(E)\rangle. \tag{3.41}$$

Here $G^-(E)$ is the incoming-wave scattering Green's function in eq. (3.30), $|\phi_f(E)\rangle$ is an energy-normalised regular solution of the Schrödinger equation for the free photofragments in channel f, and $V_f = H - H_f$ is the corresponding interaction potential. The regular wavefunction $|\phi_f(E)\rangle$ can be represented explicitly (in the simple case where there is no orbital angular momentum) as

$$\langle R_f\,|\,\phi_f(E)\rangle = \left(\frac{2\mu_f}{\pi\hbar^2 k_f}\right)^{1/2} \sin(k_f R_f)\,|\phi_f\rangle \tag{3.42}$$

where $|\phi_f\rangle$ is the internal quantum state of the photofragments in channel f and $k_f = \sqrt{2\mu_f(E-\mathcal{E}_f)}/\hbar$ is the channel wavevector.

Substituting eq. (3.41) into the integral in eq. (3.40) gives

$$\begin{aligned}\langle \psi_f^-(E) \,|\, \chi_i \rangle &= \langle \phi_f(E) \,|\, \chi_i \rangle + \lim_{\epsilon \to 0} \langle G^-(E) V_f \, \phi_f(E) \,|\, \chi_i \rangle \\ &= \langle \phi_f(E) \,|\, \chi_i \rangle + \lim_{\epsilon \to 0} \langle \phi_f(E) \,|\, V_f G^+(E) \,|\, \chi_i \rangle \end{aligned} \tag{3.43}$$

where $G^+(E)$ is the adjoint of $G^-(E)$:

$$G^+(E) = -\frac{i}{\hbar} \int_0^\infty e^{+i(E+i\epsilon-H)t/\hbar} \, dt = (E + i\epsilon - H)^{-1} \, . \tag{3.44}$$

The first integral in eq. (3.43) can be evaluated by quadrature, because $|\chi_i\rangle$ and $|\phi_f(E)\rangle$ are both known, and the second can be evaluated using a time-dependent method based on the above expression for $G^+(E)$:

$$\langle \phi_f(E) \,|\, V_f G^+(E) \,|\, \chi_i \rangle = -\frac{i}{\hbar} \int_0^\infty e^{+iEt/\hbar} \, C_{fi}(E,t) \, dt \tag{3.45}$$

where

$$C_{fi}(E,t) = \langle \phi_f(E) \,|\, V_f \,|\chi_i(t)\rangle \tag{3.46}$$

and

$$|\chi_i(t)\rangle = e^{-i(H-i\epsilon)t/\hbar} |\chi_i\rangle \tag{3.47}$$

is the wavepacket at time t.

The time-dependent calculation of a partial absorption spectrum $P_{fi}(E) = |\langle \psi_f^-(E) \,|\, \chi_i \rangle|^2$ is therefore just as straightforward as the calculation of the total absorption spectrum $P_i(E)$ in eq. (3.21): one simply calculates the correlation function $C_{fi}(E,t)$ as the wavepacket evolves and then Fourier transforms it to obtain the "hard part" of the Franck-Condon overlap integral $\langle \psi_f^-(E) \,|\, \chi_i \rangle$.

This is all we shall have time to say about partial absorption cross sections. (A more detailed discussion can be found in Schinke's book [1].) In the next lecture, we shall describe how the formal equations of this lecture can be converted into numerical methods for calculating photodissociation cross sections and then end with some illustrative examples of resonances and recurrences in the photodissociation dynamics of triatomic molecules.

4 Numerical Methods and Examples

Recall the three main equations for the time-dependent calculation of an absorption spectrum

$$P_i(E) = \lim_{\epsilon \to 0} \frac{1}{\pi\hbar} \mathrm{Re} \int_0^\infty e^{+iEt/\hbar} C_i(t)\, dt \tag{4.1}$$

where

$$C_i(t) = \langle \chi_i \,|\, e^{-i(H-i\epsilon)t/\hbar} \,|\, \chi_i \rangle \tag{4.2}$$

and

$$|\chi_i\rangle = \mu_{fi} \cdot \mathbf{e}\, |\psi_i\rangle. \tag{4.3}$$

We shall begin this lecture by showing how appropriate representations of the Hamiltonian H and the convergence parameter $-i\epsilon$ can be used to convert these equations into a numerical method, and we shall end it with some example applications to the photodissociation of triatomic molecules.

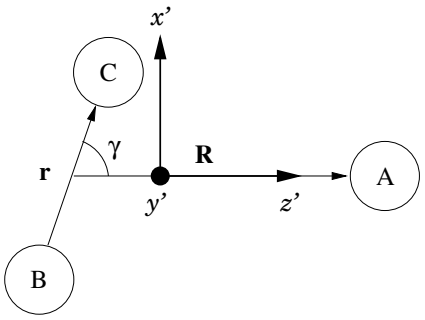
4.1 Representation of H

It is well established how to set up a matrix representation of the Hamiltonian H for any triatomic or tetratomic molecule of interest. In the terminology of Light and co-workers [14], one can use either a variational basis representation (VBR) or a discrete variable representation (DVR) in each degree of freedom. Both of these representations have their advantages, and the best one to use depends on the circumstances. We shall therefore illustrate both approaches by considering the case of a triatomic molecule in which the angular coordinates are represented in a VBR and the radial coordinates are represented in a DVR.

An appropriate Hamiltonian H for a triatomic molecule ABC is

$$H = -\frac{\hbar^2}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r}\frac{\partial^2}{\partial r^2} + \frac{l^2}{2\mu_R R^2} + \frac{j^2}{2\mu_r r^2} + V(R, r, \gamma) \tag{4.4}$$

where R is the distance from BC to A, r is the distance from B to C, $\mu_R = m_\mathrm{A} m_\mathrm{BC}/m_\mathrm{ABC}$ and l^2 are the reduced mass and squared angular momentum operator associated with $\mathbf{R}$, $\mu_r = m_\mathrm{B} m_\mathrm{C}/m_\mathrm{BC}$ and j^2 are the reduced mass and squared angular momentum operator associated with $\mathbf{r}$, and γ is the angle between $\mathbf{R}$ and $\mathbf{r}$:



Angular VBR

A convenient set of basis functions to use to represent the angular coordinates $\hat{\mathbf{R}}$ and $\hat{\mathbf{r}}$ are the body-fixed axes (BF) functions [15,16]

$$\mathcal{Y}^{JM}_{jk}(\hat{\mathbf{R}},\hat{\mathbf{r}}) = \mathcal{Y}^{JM}_{jk}(\gamma,\Omega) = \left(\frac{2J+1}{4\pi}\right)^{\frac{1}{2}} Y_{jk}(\gamma,0)\, D^{J}_{kM}(\Omega) \tag{4.5}$$

where $\Omega = (\Psi,\Theta,\Phi)$ are the Euler angles which take the space-fixed axes onto the body-fixed axes shown above (Θ and Φ are the spherical polar angles of $\mathbf{R}$ in the original space-fixed axis system and Ψ is a right-hand axis twist about $\mathbf{R}$ which brings $\mathbf{r}$ into the $x'z'$ plane) and D^{J}_{kM} is a Wigner D function in the passive convention used by Pack [15,16].

These functions are simultaneous orthonormal eigenfunctions of the commuting angular momentum operators $J^2 = (\mathbf{j}+\mathbf{l})^2$, j^2, J_z, $J_{z'}$ and $j_{z'}$, where $J_{z'}$ and $j_{z'}$ are the operators for the projection of $\mathbf{J}$ and $\mathbf{j}$ on the body-fixed z' axis along $\mathbf{R}$:

$$J^2\, \mathcal{Y}^{JM}_{jk} = \hbar^2\, J(J+1)\, \mathcal{Y}^{JM}_{jk} \tag{4.6}$$

$$j^2\, \mathcal{Y}^{JM}_{jk} = \hbar^2\, j\,(\,j+1)\, \mathcal{Y}^{JM}_{jk} \tag{4.7}$$

$$J_z\, \mathcal{Y}^{JM}_{jk} = \hbar\, M\, \mathcal{Y}^{JM}_{jk} \tag{4.8}$$

$$J_{z'}\, \mathcal{Y}^{JM}_{jk} = \hbar\, k\, \mathcal{Y}^{JM}_{jk} \tag{4.9}$$

$$j_{z'}\, \mathcal{Y}^{JM}_{jk} = \hbar\, k\, \mathcal{Y}^{JM}_{jk} \tag{4.10}$$

$$\int\int \mathcal{Y}^{J'M'}_{j'k'}(\gamma,\Omega)^{*} \mathcal{Y}^{JM}_{jk}(\gamma,\Omega)\, \sin\gamma\, d\gamma\, d\Omega = \delta_{J'J}\delta_{M'M}\delta_{j'j}\delta_{k'k}. \tag{4.11}$$

The main advantage of the BF functions is that they lead to a very simple representation of the potential energy operator

$$V(R,r)_{j'k',jk} = \int\int \mathcal{Y}^{JM}_{j'k'}(\gamma,\Omega)^* V(R,r,\gamma)\, \mathcal{Y}^{JM}_{jk}(\gamma,\Omega) \sin\gamma \, d\gamma \, d\Omega$$
$$= 2\pi\, \delta_{k'k} \int_0^\pi Y_{j'k}(\gamma,0)^* V(R,r,\gamma)\, Y_{jk}(\gamma,0) \sin\gamma d\gamma \qquad (4.12)$$

where the simplification in the second line comes from integrating out the Euler angles Ω that define the orientation of the triatomic triangle in space. The final one-dimensional integral over γ in eq. (4.12) can be done numerically by quadrature.

The representation of the rotational angular momentum operator j^2 is also trivial in view of eq. (4.7). This leaves the orbital angular momentum operator l^2, the matrix elements of which can be evaluated using the ladder equations

$$J_\pm \, D^J_{kM}(\Omega) = C^\pm_{Jk} \, D^J_{k\pm 1M}(\Omega) \qquad (4.13)$$

where

$$J_\pm = J_{x'} \mp i J_{y'} \qquad (4.14)$$

and

$$j_\pm \, Y_{jk}(\gamma,0) = C^\pm_{jk} \, Y_{jk\pm 1}(\gamma,0) \qquad (4.15)$$

where

$$j_\pm = j_{x'} \pm i j_{y'} \qquad (4.16)$$

with

$$C^\pm_{AB} = \hbar[\, A(A+1) - B(B\pm 1)\,]^{\frac{1}{2}}. \qquad (4.17)$$

(The difference between $J_\pm$ and $j_\pm$ in eqs. (4.14) and (4.16) arises because $\mathbf{J}$ is an external angular momentum whose components $(J_{x'}, J_{y'}, J_{z'})$ relative to body-fixed axes satisfy anomalous commutation relations $\mathbf{J} \wedge \mathbf{J} = -i\hbar\mathbf{J}$ whereas $\mathbf{j}$ is an internal angular momentum whose components $(j_{x'}, j_{y'}, j_{z'})$ satisfy the ordinary angular momentum commutation relations $\mathbf{j} \wedge \mathbf{j} = +i\hbar\mathbf{j}$.) Hence:

$$\left(l^2\right)^J_{j'k',jk} = \langle JMj'k' \,|\, (\mathbf{J}-\mathbf{j})^2 \,|\, JMjk\rangle$$
$$= \langle JMj'k' \,|\, J^2 + j^2 - 2\mathbf{J}\cdot\mathbf{j} \,|\, JMjk\rangle$$
$$= \langle JMj'k' \,|\, J^2 + j^2 - 2J_{z'}j_{z'} - J_+j_+ - J_-j_- \,|\, JMjk\rangle$$
$$= \delta_{j'j}[\, D_{Jjk}\delta_{k'k} - C^+_{Jk}C^+_{jk}\delta_{k'k+1} - C^-_{Jk}C^-_{jk}\delta_{k'k-1}\,] \qquad (4.18)$$

where

$$D_{Jjk} = \hbar^2 \, [\, J(J+1) + j(j+1) - 2k^2 \,]. \tag{4.19}$$

Parity under the coordinate inversion $\hat{\mathbf{R}} \rightarrow -\hat{\mathbf{R}}$ and $\hat{\mathbf{r}} \rightarrow -\hat{\mathbf{r}}$ can also be exploited by defining parity-adapted linear combinations of the BF angular functions in eq. (4.5), and this final nicety is worth implementing in practical calculations because it reduces the range of the helicity quantum number k from $-\min(J,j) \ldots +\min(J,j)$ to $0 \ldots \min(J,j)$ in one parity block and $1 \ldots \min(J,j)$ in the other [15,16].

Radial DVR

One of the simplest ways to represent the radial coordinate R is to use a particle-in-a-box DVR in a finite interval $0 \leq R \leq R_{\max}$ [17]. This DVR involves a set of $n_R - 1$ equally spaced grid points

$$R_p = p \, \Delta R \quad \text{for } p = 1, 2, \ldots n_R - 1 \tag{4.20}$$

where ΔR is the grid spacing

$$\Delta R = R_{\max}/n_R. \tag{4.21}$$

The grid representation of the radial kinetic energy operator is

$$\left(-\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} \right)_{p'p} = -\frac{\hbar^2}{2\mu_R} \, \Delta R \sum_{n=1}^{n_R - 1} \phi_n(R_{p'}) \, \phi_n''(R_p) \tag{4.22}$$

where $\phi_n(R)$ is the n-th particle-in-a-box eigenfunction

$$\phi_n(R) = (2/R_{\max})^{\frac{1}{2}} \sin\left(n\pi R/R_{\max}\right). \tag{4.23}$$

Colbert and Miller have shown how the sum in eq. (4.22) can be worked out analytically with these functions to give [17]

$$\left(-\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} \right)_{p'p} = \frac{\hbar^2}{2\mu_R} \frac{\pi^2}{2R_{\max}^2} \begin{cases} (2n_R^2 + 1)/3 - S_{2p} & \text{if } p' = p \\ S_{p'-p} - S_{p'+p} & \text{if } p' \neq p \end{cases} \tag{4.24}$$

where

$$S_k = (-1)^k / \sin^2(k\pi/2n_R) \quad \text{for } k = 1, 2, \ldots 2(n_R - 1). \tag{4.25}$$

The corresponding representation of the potential energy operator is simply

$$V(r,\gamma)_{p'p} = \delta_{p'p} V(R_p, r, \gamma) \tag{4.26}$$

and a similar representation can also be used for the other radial coordinate r in eq. (4.4).

The above equations can therefore be combined to obtain a matrix representation of the Hamiltonian H in eq. (4.4) in which the angular coordinates $\hat{\mathbf{R}}$ and $\hat{\mathbf{r}}$ are represented in a VBR and the radial coordinates R and r are represented in a DVR:

$$\begin{aligned} H^J_{p'q'j'k',pqjk} &= (T_R)_{p'p}\,\delta_{q'q}\delta_{j'j}\delta_{k'k} + (T_r)_{q'q}\,\delta_{p'p}\delta_{j'j}\delta_{k'k} \\ &\quad + \frac{(l^2)^J_{jk',jk}}{2\mu_R R_p^2}\delta_{p'p}\delta_{q'q}\delta_{j'j} + \frac{\hbar^2\, j(j+1)}{2\mu_r r_q^2}\delta_{p'p}\delta_{q'q}\delta_{j'j}\delta_{k'k} \\ &\quad + V(R_p, r_q)_{j'k,jk}\delta_{p'p}\delta_{q'q}\delta_{k'k}. \end{aligned} \tag{4.27}$$

Notice in particular the sparsity of the representation, and the fact that the term involving l^2 is the only one that depends on the total angular momentum quantum number J. Similar mixed (radial DVR and angular VBR) representations can also be derived for tetratomic molecules.

4.2 Representation of $-i\epsilon$

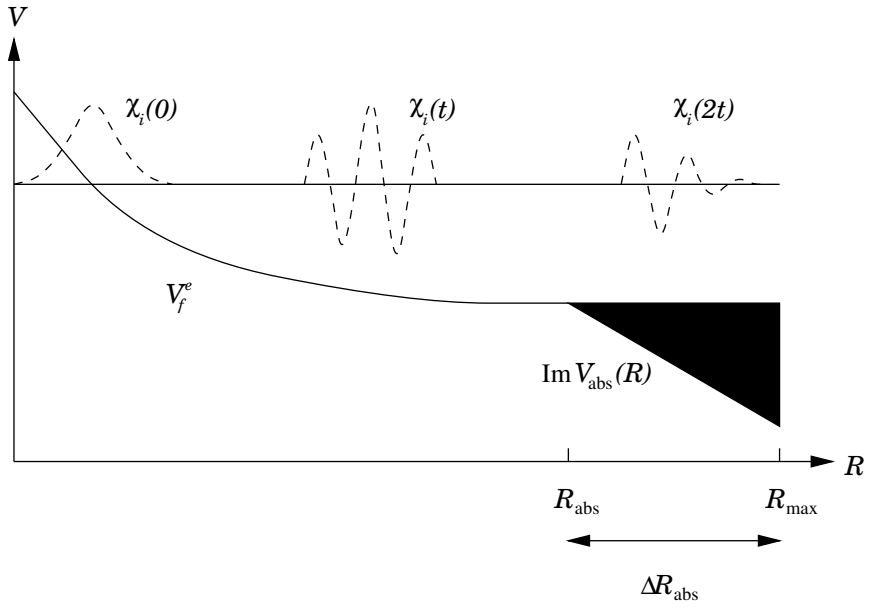
Now consider the factor $e^{-\epsilon t}$ in eq. (4.2), which guarantees the convergence of the integral over t in eq. (4.1). The question is how best to represent this factor on a finite grid, and the usual solution to this problem is to regard

$$V_{\text{abs}} = -i\epsilon \tag{4.28}$$

as a coordinate-dependent absorbing potential which absorbs the wavepacket

$$|\chi_i(t)\rangle = e^{-i(H-i\epsilon)t/\hbar}\,|\chi_i(0)\rangle \tag{4.29}$$

as it approaches the boundary of the grid. Since all of the wavepacket will eventually reach the boundary of the grid in a continuum problem this guarantees the convergence of the time integral, and since the absorbing potential can be taken to be zero in the interaction region it also corresponds (in a practical sense) to taking the limit as $\epsilon \to 0$ in eq. (4.1). (See also Miller's discussion of the rôle of $-i\epsilon$ in time-independent reaction rate theory.)



It is not difficult to construct such an absorbing potential. For example, Neuhauser and Baer [18], Child [19], and Seideman and Miller [20] have all shown (in different ways) that the simple negative imaginary potential

$$V_{\rm abs}(R) = -iV_I\,(R - R_{\rm abs})/\Delta R_{\rm abs} \tag{4.30}$$

where

$$\Delta R_{\rm abs} = R_{\rm max} - R_{\rm abs} \tag{4.31}$$

will be effective in absorbing the components of the wavepacket with translational energies E_t that satisfy

$$E_t^{\frac{1}{2}}/C \le V_I \le C\,E_t^{\frac{3}{2}} \tag{4.32}$$

where

$$C = (2\mu_R/\hbar^2)^{\frac{1}{2}}\Delta R_{\rm abs}/10 \tag{4.33}$$

and the numerical factor of 10 in the denominator of eq. (4.33) guarantees 99% absorption according to Child's analysis [19].

The first inequality in eq. (4.32) arises because the absorbing potential must be strong enough to give complete absorption over the range $\Delta R_{\rm abs}$ and

the second arises because it must also turn on slowly enough to avoid any appreciable reflection. Both inequalities can be satisfied by making $\Delta R_{\rm abs}$ large enough, and it follows in particular from eqs (4.32) and (4.33) that $\Delta R_{\rm abs}$ must be larger than the de Broglie wavelength at E_t:

$$\Delta R_{\rm abs} \geq (5/\pi)\lambda \tag{4.34}$$

where

$$\lambda = h/(2\mu_R E_t)^{\frac{1}{2}}. \tag{4.35}$$

The lesson to be learned from this is that the low translational energy components of the wavepacket are more difficult to absorb than the high translational energy components, because they correspond to longer de Broglie wavelengths λ and hence require larger absorbing regions $\Delta R_{\rm abs}$. This lesson is also independent of the form chosen for the negative imaginary potential, because Seideman and Miller's analysis [20] shows that $\Delta R_{\rm abs}$ must be larger than λ for the more general absorbing potential

$$V_{\rm abs}(R) = -iV_I\,[\,(R - R_{\rm abs})/\Delta R_{\rm abs}\,]^n\,. \tag{4.36}$$

In practice, the absorbing potentials in eqs (4.30) and (4.36) can be made to work well despite the difficulty with low translational energies, and they have been used in a great many successful calculations. In order to apply these potentials to the triatomic problem considered in section 4.1 one simply has to note that the molecule can (in general) dissociate along either of the radial directions R or r, so the appropriate mixed (angular VBR and radial DVR) representation of $-i\epsilon$ is

$$(-i\epsilon)_{p'q'j'k',pqjk} = [\,V_{\rm abs}(R_p) + V_{\rm abs}(r_q)\,]\;\delta_{p'p}\delta_{q'q}\delta_{j'j}\delta_{k'k} \tag{4.37}$$

where $V_{\rm abs}(r)$ is defined similarly to $V_{\rm abs}(R)$ (although perhaps with different parameters V_I and $\Delta r_{\rm abs}$).

4.3 Wavepacket propagation

The only remaining problem is how to evolve the initial wavepacket $|\,\chi_i(0)\rangle$ to give $|\,\chi_i(t)\rangle$ as in eq. (4.29). A large number of different methods have been proposed for this purpose [12], but here we shall simply discuss what is generally regarded as being the best one to use for a time-independent Hamiltonian [21]:

The Chebyshev method

This method is based on the Chebyshev polynomial expansion of $e^{-i\omega t}$

$$e^{-i\omega t} = \sum_{n=0}^{\infty} a_n(t)\, T_n(\omega) \tag{4.38}$$

where

$$a_n(t) = \frac{(2-\delta_{n0})}{\pi} \int_{-1}^{1} \frac{e^{-i\omega t} T_n(\omega)}{(1-\omega^2)^{1/2}}\, d\omega = (2-\delta_{n0})(-i)^n J_n(t). \tag{4.39}$$

(The first equality in eq. (4.39) follows from the orthogonality of the Chebyshev polynomials $T_n(\omega)$ and the second follows from the expression for the Fourier transform of the Bessel function $J_n(t)$ in eq. (11.4.24) of Abramowitz and Stegun [9].)

Equation (4.38) only holds for $-1 < \omega < 1$, but it is easy to scale it to the range $a < x < b$:

$$e^{-ixt} = e^{-i\overline{x}t} \sum_{n=0}^{\infty} a_n(\Delta x t)\, T_n(\omega) \tag{4.40}$$

where

$$\overline{x} = (b+a)/2 \tag{4.41}$$

and

$$\Delta x = (b-a)/2 \tag{4.42}$$

and

$$\omega = (x - \overline{x})/\Delta x. \tag{4.43}$$

Moreover this scaled version can be applied directly to the evolution operator $\exp(-iHt/\hbar)$ (ignoring for simplicity the effect of the imaginary convergence factor $-i\epsilon$) by interpreting x as the hermitian operator $x = H/\hbar$ and $\hbar a$ and $\hbar b$ as the lowest ($E_{\min}$) and highest ($E_{\max}$) eigenvalues of H (in a matrix representation like eq. (4.27)):

$$e^{-iHt/\hbar} = e^{-i\overline{E}t/\hbar} \sum_{n=0}^{\infty} a_n(\Delta E t/\hbar)\, T_n(H_{\rm norm}) \tag{4.44}$$

where

$$\overline{E} = (E_{\max} + E_{\min})/2 \tag{4.45}$$

and

$$\Delta E = (E_{\max} - E_{\min})/2 \tag{4.46}$$

and

$$H_{\rm norm} = (H - \overline{E})/\Delta E. \tag{4.47}$$

The expansion coefficient $a_n(\Delta E t/\hbar)$ in eq. (4.44) is given by eq. (4.39) as

$$a_n(\Delta E t/\hbar) = (2 - \delta_{n0})(-i)^n J_n(\Delta E t/\hbar) \tag{4.48}$$

and since the Bessel function $J_n(\Delta E t/\hbar)$ decreases exponentially with increasing n beyond $n = \Delta E t/\hbar$ one can replace eq. (4.44) to a very good approximation with

$$e^{-iHt/\hbar} \simeq e^{-i\overline{E}t/\hbar} \sum_{n=0}^{N} a_n(\Delta E t/\hbar)\, T_n(H_{\rm norm}) \tag{4.49}$$

where (for example)

$$N = [\Delta E t_{\max}/\hbar] + 10. \tag{4.50}$$

Equation (4.49) is the central equation of the Chebyshev propagation method [21]. In order to apply it to the evolution of a wavepacket one can use the recursion relation satisfied by the Chebyshev polynomials to write

$$|\chi_i(t)\rangle = e^{-iHt/\hbar}|\chi_i(0)\rangle \simeq e^{-i\overline{E}t/\hbar} \sum_{n=0}^{N} a_n(\Delta E t/\hbar)\, |\chi_n\rangle \tag{4.51}$$

where

$$|\chi_n\rangle = T_n(H_{\rm norm})\, |\chi_i(0)\rangle \tag{4.52}$$

gives

$$|\chi_0\rangle = |\chi_i(0)\rangle \tag{4.53}$$

$$|\chi_1\rangle = H_{\rm norm}\, |\chi_0\rangle \tag{4.54}$$

and

$$|\chi_{n+1}\rangle = 2H_{\rm norm}\, |\chi_n\rangle - |\chi_{n-1}\rangle \quad \text{for } n = 1, 2, \ldots N-1. \tag{4.55}$$

Each of the last N terms in eq. (4.51) can thus be evaluated with one application of the scaled Hamiltonian $H_{\rm norm}$ in eq. (4.47) on a state vector, and

this is greatly facilitated (in the triatomic case) by exploiting the sparsity of the mixed (angular VBR and radial DVR) representation of H in eq. (4.27).

The general features of the Chebyshev method are that it is capable of very high accuracy (because the errors are distributed almost perfectly uniformly over the spectrum $E_{\min} < H < E_{\max}$ of H) and it is also very efficient when properly applied [12]. However, in order to apply it properly it is *essential* to make ΔE in eq. (4.46) as small as possible (bearing in mind the range of energies contained in the initial wavepacket) in order to reduce the required value of N in eq. (4.50). This is also possible to arrange using the mixed representation of H in eq. (4.27), but it requires a few dirty tricks (like shelving the potential at a cut-off $V_{\max}$ and restricting the range of the rotational angular momentum quantum number j to a value $j_{\max}(R_p, r_q, J)$ that depends on R_p, r_q and J) which have to be implemented fairly carefully.

4.4 Examples

There would be little point to these lectures if photodissociation dynamics were not very interesting. Therefore, to end this lecture course, here are two contrasting examples of indirect photodissociation which make it all worthwhile. The quantum mechanical parts of both of these examples can be reproduced (if you want to do this) using the numerical methods described above.

Diffuse structure in the photodissociation of CO_2

This example concerns the recently solved problem of how to assign diffuse vibrational structure in molecular photodissociation spectra [5,22-24]. Figures 1 and 2 show the modulus of the autocorrelation function $|C_i(t)|$ and the corresponding absorption spectrum $P_i(E)$ that are obtained in the standard collinear model for the photodissociation of CO_2 [22,23]. The weak recurrences in $C_i(t)$ give rise to diffuse vibrational structure in $P_i(E)$ for reasons explained in lecture 3. The first few recurrences occur at the periods of the classical periodic orbits shown in Figure 3 [22,23], and indeed the dynamics can be linearised semiclassically around each of these periodic orbits to give the corresponding contribution to $|C_i(t)|$ as shown in Figure 4 [24]. The way to "assign" diffuse vibrational structure is therefore simply to identify the relevant classical periodic orbits:

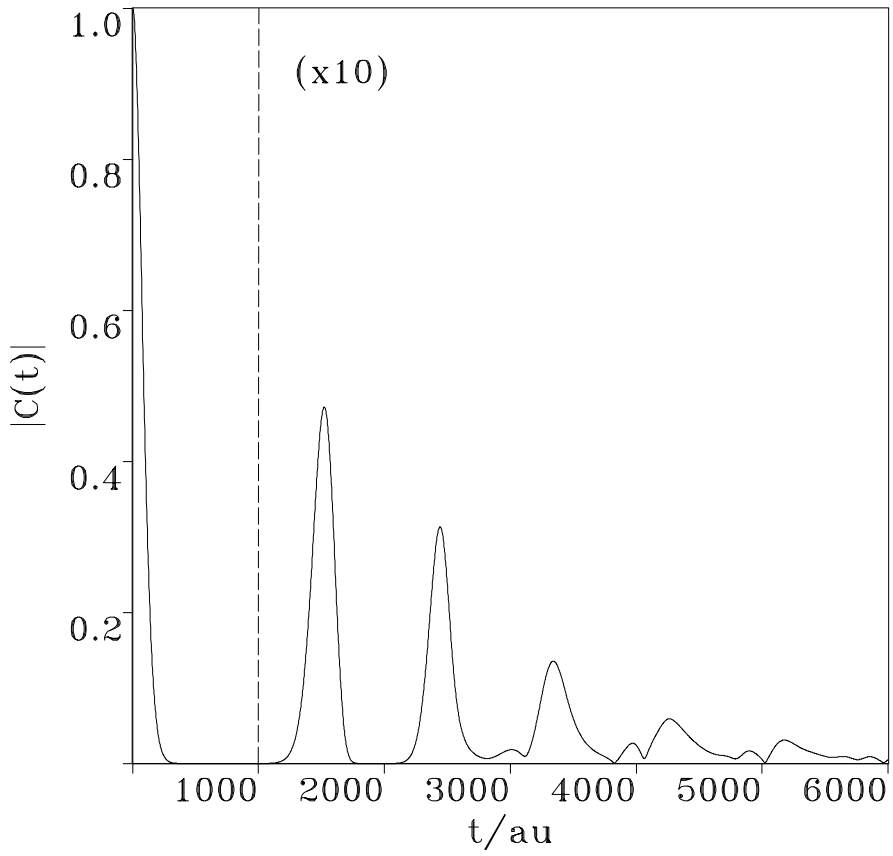


Figure 1: The modulus of the autocorrelation function $|C_i(t)|$ versus t for the standard collinear model for the photodissociation of CO_2 [22,23]. Note that the recurrences beyond $t = 1000$ au have been multiplied by 10, and are therefore really far weaker than shown.

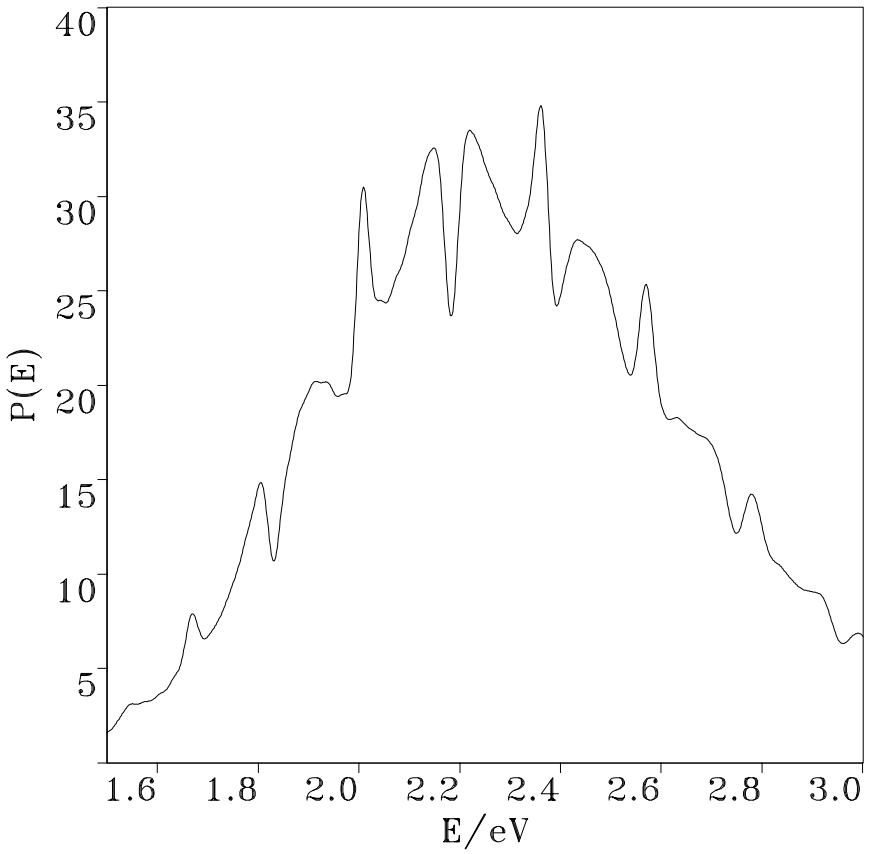


Figure 2: The photodissociation spectrum $P_i(E)$ versus E for the standard collinear model for the photodissociation of CO_2 [22,23]. This is an example of the diffuse vibrational structure discussed in lecture 3, which arises because of the weak recurrences in $|C_i(t)|$ in Figure 1.

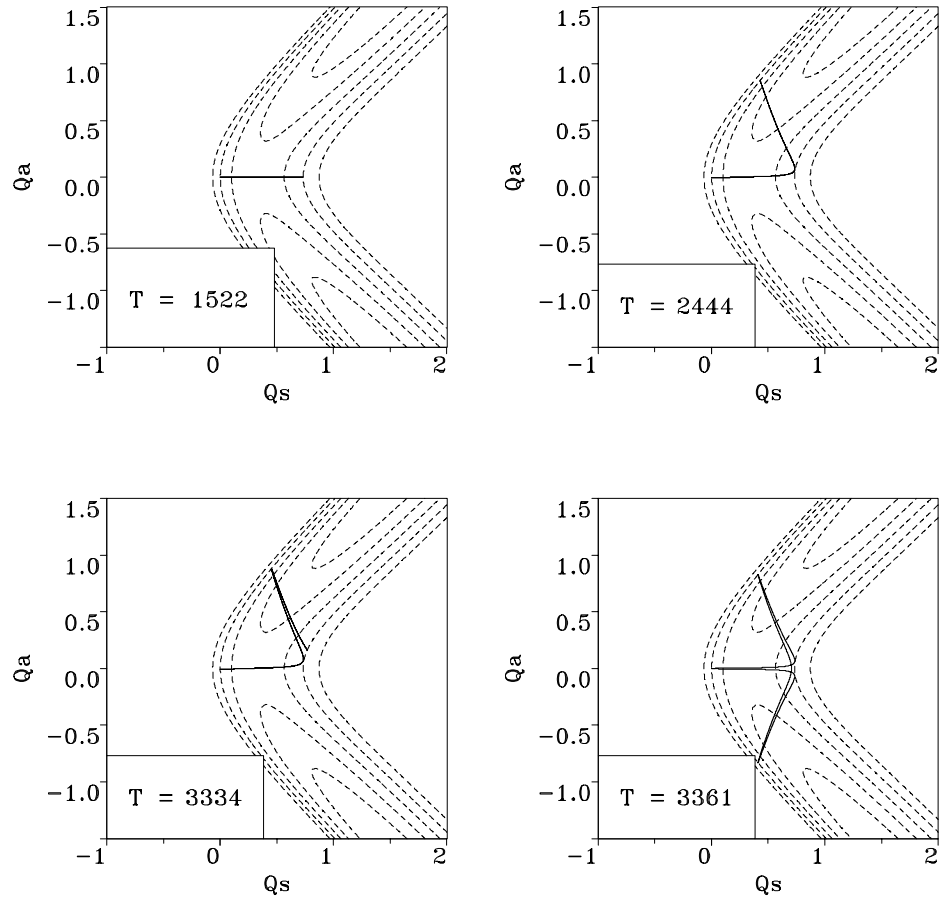


Figure 3: Classical periodic orbits on the excited (LEPS) potential energy surface in the standard collinear model for the photodissociation of CO_2 [22,23]. The periods of these orbits coincide almost exactly with the times of the first few recurrences in $|C_i(t)|$ in Figure 1.

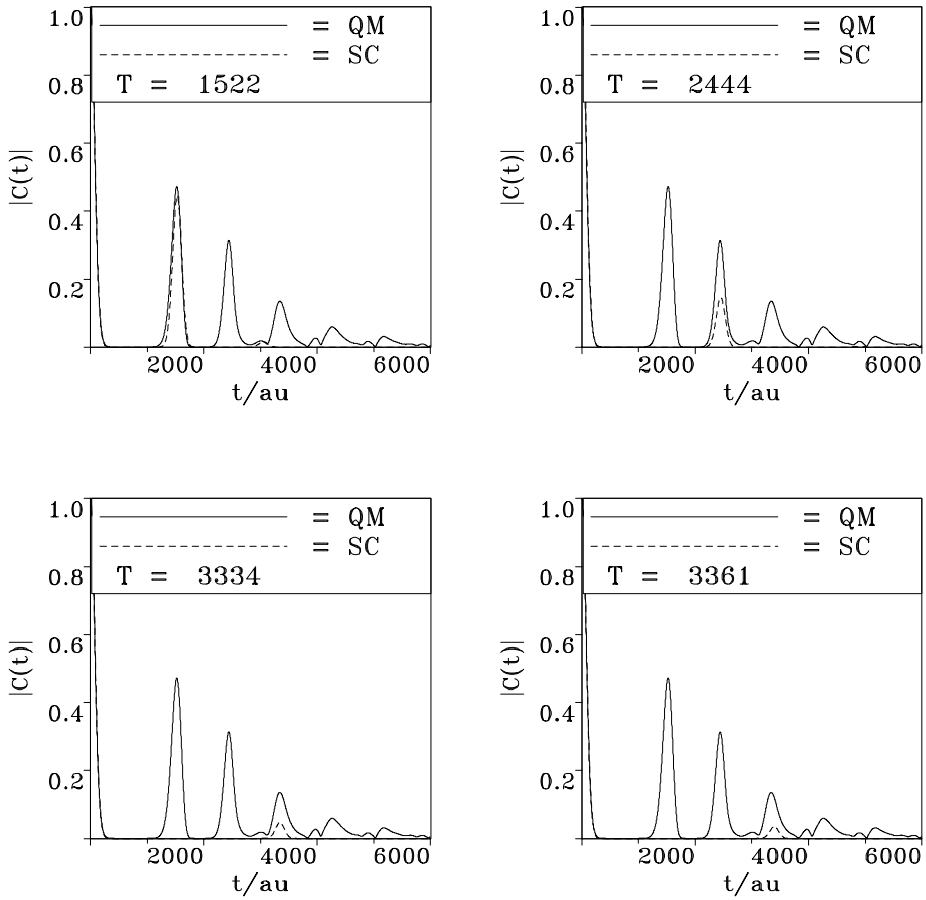


Figure 4: Semiclassical contributions from each of the periodic orbits in Figure 3 to the modulus of the correlation function $|C_i(t)|$ in Figure 1 [24]. Note that the curves have again been multiplied by 10 beyond $t = 1000$ au for clarity. The semiclassical contribution to the first recurrence at $t = 1522$ au clearly agrees extremely well with the exact quantum mechanical result. The semiclassical contribution to the second recurrence at $t = 2444$ au agrees equally well when it is multiplied by a factor of 2 to account for the fact that there are two equivalent classical orbits with this period which return to the Franck-Condon region in phase, and similarly (although in this case the situation is complicated by interference) for the following two periodic orbits [24].

Resonances in the photodetachment of FH_2^-

This example concerns the long-standing debate about the importance of quantum mechanical resonances in chemical reactions [13]. Figure 5 shows a Franck-Condon simulation of the photoelectron spectrum $P_i(E)$ of the para FH_2^- anion at the 1 meV energy resolution that one might expect to be attainable in an anion threshold photodetachment experiment [25]. The anion photodetaches to the transition state region of the neutral $F+H_2$ reaction and the photoelectron spectrum therefore probes the dynamics of the neutral reaction in this transition state region [26].

The spectrum consists of a sequence of three broad peaks with several rather narrower peaks superimposed. Such a spectrum can be assigned by noting that $P_i(E)$ in eq. (4.1) can be re-written as

$$P_i(E) = \langle \chi_i \,|\, \chi_i(E) \rangle \tag{4.56}$$

where

$$|\chi_i(E)\rangle = \frac{1}{\pi\hbar} \mathrm{Re} \int_0^\infty e^{+iEt/\hbar} \, |\chi_i(t)\rangle \, dt \tag{4.57}$$

is an energy-dependent scattering wavefunction that can be computed from the evolving wavepacket: the assignment can therefore be made by examining the nodal structure of $|\chi_i(E)\rangle$ at each peak energy E. (However, it is found in practice that it is easier to look at the nodal structure of

$$|\chi_i''(E)\rangle = -\frac{1}{\pi\hbar^3} \mathrm{Re} \int_0^\infty t^2 \, e^{+iEt/\hbar} \, |\chi_i(t)\rangle \, dt \tag{4.58}$$

which allows one to assign narrow peaks rather more easily [25].)

For example, Figure 6 shows the wavefunctions $|\chi_i''(E)\rangle$ at the energies of the first three peaks in Figure 5. The first and third peaks are clearly due to quasi-bound resonance states localised in the van der Waals well regions of the $F+H_2$ reactant and H+HF product valleys shown in Figure 7, whereas the second broader peak is due to a delocalised direct scattering state [25]. The narrow peaks in Figure 5 can thus be attributed to reactive scattering resonances, which is interesting because these resonances have yet to be detected experimentally [27]. Figure 5 suggests that a threshold photodetachment experiment on the FH_2^- anion will resolve them very clearly and unambiguously:

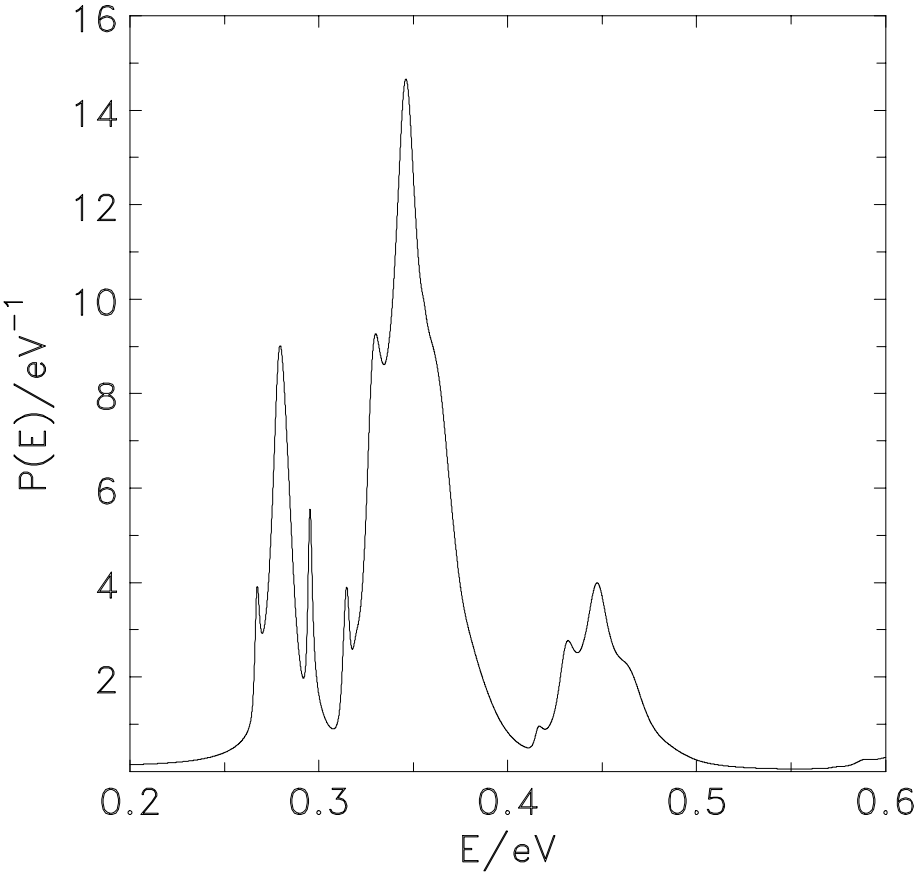


Figure 5: Franck-Condon simulation of the photoelectron spectrum $P_i(E)$ of para FH_2^- at 1 meV (full width at half maximum) energy resolution [25].

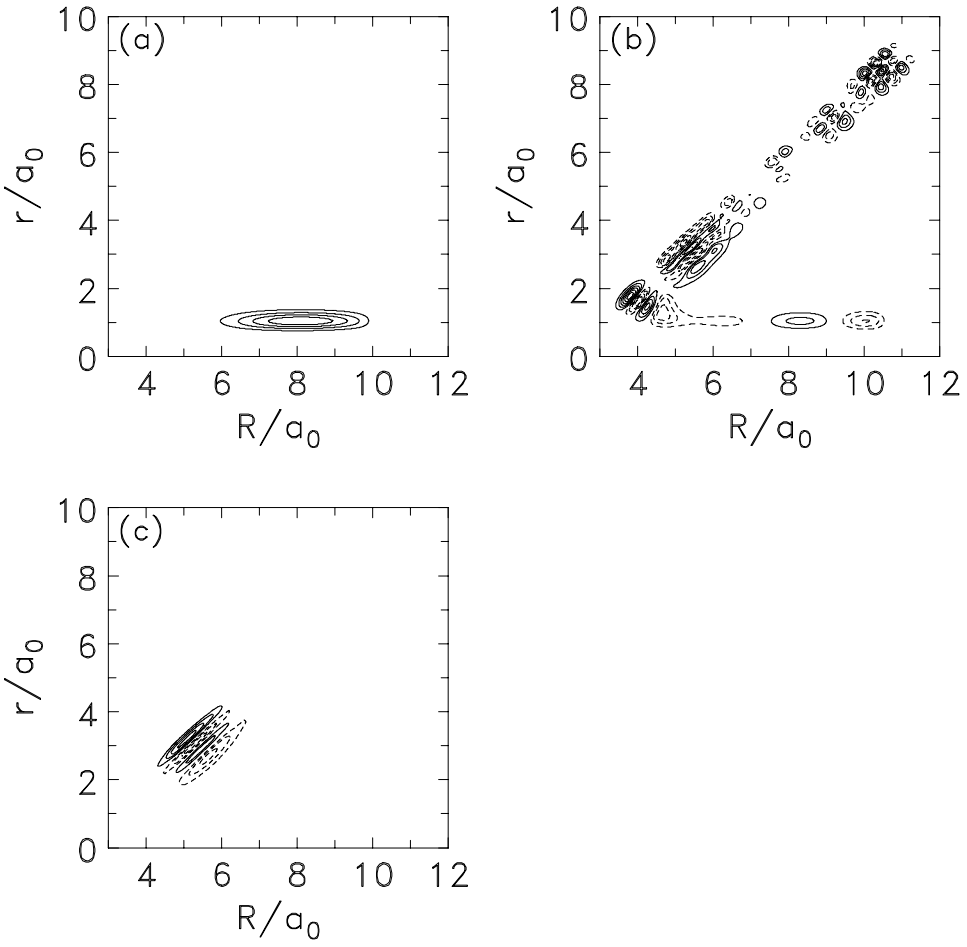


Figure 6: (a) A quasi-bound resonance state in the reactant valley of the $F+H_2$ reaction at $E = 0.268$ eV, (b) a direct scattering state at $E = 0.280$ eV and (c) a quasi-bound resonance state in the product valley at $E = 0.294$ eV [25]. (The coordinates of the plots are the mass-scaled Jacobi coordinates R and r of the $F+H_2$ reactant arrangement.)

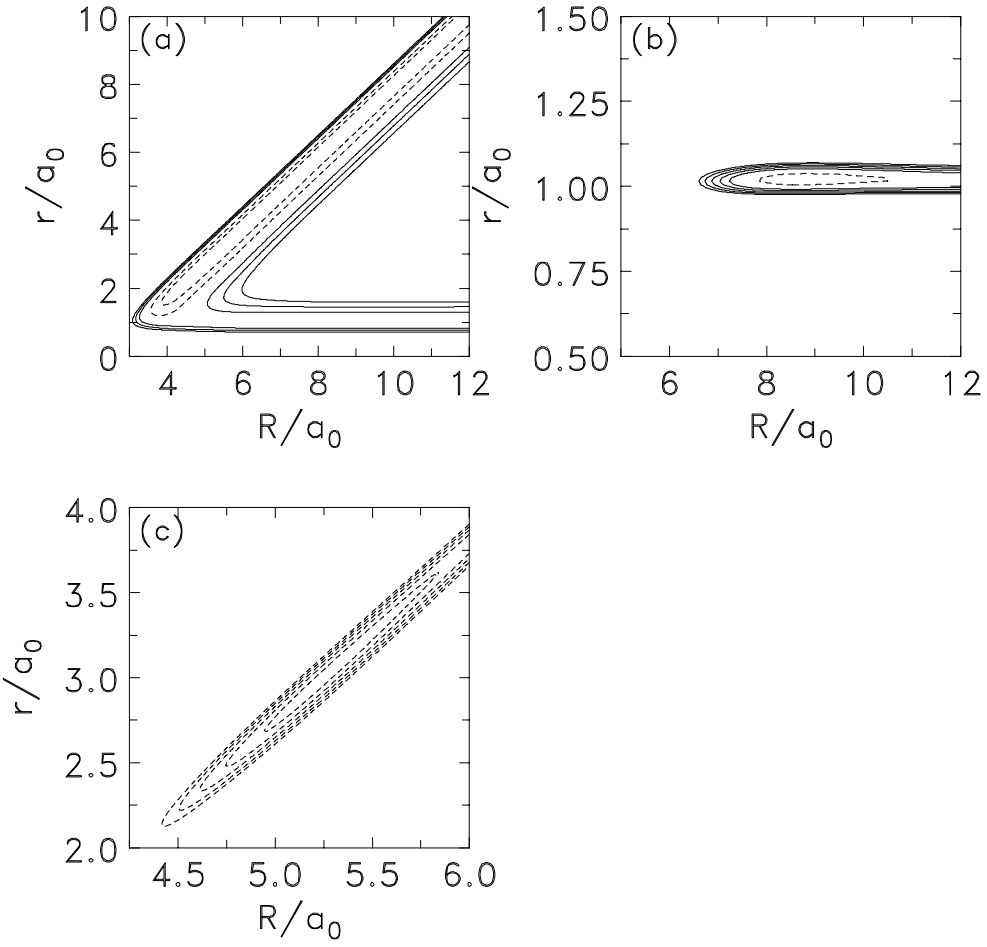


Figure 7: (a) Collinear contour plot of the Stark-Werner $F+H_2$ potential energy surface [28], with expansions of the reactant and product van der Waals well regions in panels (b) and (c). Solid contours correpond to positive energies and dashed contours to negative energies relative to the bottom of the asymptotic $F+H_2$ reactant valley.

5 References and Further Reading

5.1 Books

[1] R.Schinke, Photodissociation Dynamics (Cambridge University Press, Cambridge, 1993) – for everything in it.

[2] B.I.Bleaney and B.Bleaney, Electricity and Magnetism (3rd Edition, Oxford University Press, Oxford, 1976) – for Maxwell's equations and the energy density of electromagnetic radiation.

[3] P.A.M.Dirac, The Principles of Quantum Mechanics (4th Edition, Oxford University Press, Oxford, 1958) – for translational eigenstates, delta functions, and a chapter on the quantum mechanical theory of radiation (not discussed here).

[4] E.Fermi, Nuclear Physics (University of Chicago Press, Chicago, 1950) – for Fermi's Golden Rule (the one used here is "Golden Rule No. 2" – see p. 142).

[5] G.Herzberg, Molecular Spectra and Molecular Structure Vols. I-III (Van Nostrand-Reinhold, New York, 1945) – for everything you could possibly want to know about spectroscopy and more. (The diffuse vibrational structure in the absorption spectrum of CO_2 is discussed on p. 500 of Volume III.)

[6] R.N.Zare, Angular Momentum (Wiley, New York, 1988) – for a clear discussion of spherical tensor operators and the Wigner-Eckart theorem (in chapter 5).

[7] D.M.Brink and G.R.Satchler, Angular Momentum (3rd Edition, Oxford University Press, Oxford, 1993) – ditto (in chapter 4). See also the reduction formula in eq. (2.30).

[8] R.G.Newton, Scattering Theory of Waves and Particles (McGraw-Hill, New York, 1966) – for continuum wavefunctions and the Lippmann-Schwinger equation.

[9] M.Abramowitz and I.A.Stegun, Handbook of Mathematical Functions (Dover, New York, 1965) – for eqs. (11.4.24) and (22.2.4), which are the basis of the Chebyshev propagation method.

5.2 Review Articles

[10] E.U.Condon, Am. J. Phys. 15 (1947) 365 – an early review of the Franck-Condon principle and the Condon approximation.

[11] R.G.Gordon, Adv. Magn. Res. 3 (1968) 1 – a review of correlation functions in molecular spectroscopy.

[12] C.Leforestier *et al.*, J. Comput. Phys. 94 (1991) 59 – a review of wavepacket propagation methods.

[13] G.C.Schatz, Ann. Rev. Phys. Chem. 39 (1988) 317 – a review of resonances in chemical reactions (and why they are difficult to observe).

5.3 Research Papers

[14] J.V.Lill, G.A.Parker and J.C.Light, Chem. Phys. Letters 89 (1982) 483 – the paper that coined the term discrete variable representation (DVR).

[15] R.T Pack, J. Chem. Phys. 60 (1973) 633 – an excellent paper on SF and BF angular basis functions for triatomic molecules.

[16] R.T Pack and G.A.Parker, J. Chem. Phys. 87 (1987) 3888 – another very useful description angular basis functions (among other things).

[17] D.T.Colbert and W.H.Miller, J. Chem. Phys. 96 (1992) 1982 – Miller's way of looking at DVRs (all the meat in this paper is in the appendix).

[18] D.Neuhauser and M.Baer, J. Chem. Phys. 90 (1989) 4351 – the first in a series of papers by these authors on absorbing potentials.

[19] M.S.Child, Mol. Phys. 72 (1991) 89 – a useful WKB (and quantum mechanical) analysis of linear absorbing potentials.

[20] T.Seideman and W.H.Miller, J. Chem. Phys. 96 (1992) 4412 – a more general WKB analysis of absorbing potentials (in appendix B – this paper is also worth reading for other reasons).

[21] H.Tal-Ezer and R.Kosloff, J. Chem. Phys. 81 (1984) 3967 – the first paper on the Chebyshev propagation method.

[22] R.Shinke and V.Engel, J. Chem. Phys. 93 (1990) 3252 – the first paper to explain the diffuse vibrational structure in the absorption spectrum of CO_2 in terms of classical periodic orbits.

[23] K.C.Kulander, C.Cerjan and A.E.Orel, J. Chem. Phys. 94 (1991) 2571 – another paper saying exactly the same thing that was submitted more-or-less simultaneously (the time was obviously right for it).

[24] O.Zobay and G.Alber, J. Phys. B 26 (1993) L539 – a really beautiful paper by two physicists on the semiclassical calculation of the absorption spectrum of CO_2 from periodic orbits. (The semiclassical calculations described here were actually done in a different way by my research student Mark Brewer, but the results are virtually identical to Zobay and Alber's.)

[25] C.L.Russell and D.E.Manolopoulos, Chem. Phys. Letters 256 (1996) 465 – how to observe the elusive resonances in $F+H_2$ reactive scattering.

[26] D.E.Manolopoulos, K.Stark, H-J.Werner, D.W.Arnold, S.E.Bradforth and D.M.Neumark, Science 262 (1993) 1852 - the transition state of the $F+H_2$ reaction.

[27] J.F.Castillo, D.E.Manolopoulos, K.Stark and H-J.Werner, J. Chem. Phys. 104 (1996) 2743 - quantum mechanical angular distributions for the $F+H_2$ reaction (including a careful analysis of the selective forward scattering of the $HF(v'=3)$ product which proves that it has nothing to do with resonances).

[28] K.Stark and H-J.Werner, J. Chem. Phys. 104 (1996) 6515 - a highly correlated ab initio potential energy surface for the $F+H_2$ reaction which made the work in refs. [25] to [27] possible.

6 Problems

1. (a) Derive eq. (1.11) from eqs. (1.5) to (1.10). (b) Verify that the plane polarised electromagnetic wave defined in eqs. (1.24) and (1.25) does indeed satisfy Maxwell's equations provided $kE_0 = \mu_0 \omega H_0$ and $kH_0 = \epsilon_0 \omega E_0$.

2. Show how the Fourier transform equations

$$F(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{+i\omega t} f(t)\, dt$$

and

$$f(t) = \int_{-\infty}^{\infty} e^{-i\omega t} F(\omega)\, d\omega$$

can be combined to obtain both the Fourier representation of the delta function in eq. (3.18) and (hence) the sinc function representation used in eq. (1.47).

3. Use the expression for the absorption cross section given in eqs. (2.1) and (2.2) to derive the sum rule

$$\int \frac{\sigma_i(\omega)}{\omega} d\omega = \frac{\pi}{\hbar \epsilon_0 c} \langle \psi_i |\ (\mu \cdot \mathbf{e})^2\ | \psi_i \rangle\,,$$

(which shows that this particular moment of the absorption cross section is independent of both the electronics and the dynamics of the final state).

4. The usual version of the Lippmann-Schwinger equation is

$$|\psi_f^+(E)\rangle = |\phi_f(E)\rangle + \lim_{\epsilon \to 0} G_f^+(E) V_f |\psi_f^+(E)\rangle$$

where

$$(E - H_f)\, |\phi_f(E)\rangle = |0\rangle$$

and

$$G_f^+(E) = (E + i\epsilon - H_f)^{-1}\,.$$

Show that this equation can be rearranged into the equivalent forms

$$|\psi_f^+(E)\rangle = \lim_{\epsilon \to 0} i G^+(E) \epsilon |\phi_f(E)\rangle$$

and

$$|\psi_f^+(E)\rangle = |\phi_f(E)\rangle + \lim_{\epsilon \to 0} G^+(E) V_f |\phi_f(E)\rangle$$

where

$$G^+(E) = (E + i\epsilon - H)^{-1}$$

with

$$H = H_f + V_f,$$

which are more useful for computation because they do not have the unknown scattering wavefunction $|\psi_f^+(E)\rangle$ on the right-hand side. [The first of these forms is used extensively by Miller and co-workers and the second is the outgoing-wave version of eq. (3.41).]

5. Show that the usual angular momentum commutation relations

$$\mathbf{J} \wedge \mathbf{J} = +i\hbar\,\mathbf{J}$$

imply the equations

$$\left[J^2, J_z\right] = 0 \qquad [J_z, J_\pm] = \pm\hbar J_\pm$$
$$\left[J^2, J_\pm\right] = 0 \qquad [J_+, J_-] = 2\hbar J_z$$

where

$$J_\pm = J_x \pm i J_y,$$

whereas the anomalous angular momentum commutation relations

$$\mathbf{J} \wedge \mathbf{J} = -i\hbar\,\mathbf{J}$$

imply the same equations with $J_\pm$ redefined as

$$J_\pm = J_x \mp i J_y$$

as in eq. (4.14).

6. Use eqs. (4.22) and (4.23) to derive Colbert and Miller's simplified expression for the grid representation of the radial kinetic energy operator in a particle-in-a-box DVR.

7. Estimate the minimum width of the absorbing region ΔR_{abs} that can be used to simulate (a) the photodissociation spectrum of CO_2 and (b) the photoelectron spectrum of FH_2^-, assuming a minimum relevant photofragment translational energy of $E_t = 10$ meV in each case. [NB: For completeness, you should consider both possible photofragment arrangements F+H_2 and H+HF in part (b).]

8. Equation 11.4.24 of Abramowitz and Stegun for the (inverse) Fourier transform of the Bessel function $J_n(t)$ is

$$\int_{-\infty}^{\infty} e^{-i\omega t} J_n(t)\, dt = \begin{cases} \frac{2(-i)^n T_n(\omega)}{(1-\omega^2)^{1/2}} & \text{if } \omega^2 < 1 \\ 0 & \text{if } \omega^2 > 1. \end{cases}$$

Use this equation to derive the expression for the Chebyshev expansion coefficient $a_n(t)$ of $e^{-i\omega t}$ given in eq. (4.39) of the lecture notes.