

Solutions to Chapter 4 Problems

1. Derivation: $\hat{H}(r, R) = \hat{T}_N(R) + \hat{H}_e(r, R)$

$$i\hbar \frac{\partial \phi}{\partial t} = \hat{H} \phi \quad (1)$$

The electronic wavefunctions satisfy $\hat{H}_e \phi_i = U_i \phi_i$, where U_i is the electronic energy of the i^{th} state.

N.B. Solutions differ at each set of nuclear coordinates.

Now, expand the total wavefunction as the product of the electronic wavefunctions ϕ_i , and the nuclear wavefunctions ψ_i .

$$\Phi = \sum_i \psi_i \phi_i$$

Substitute this back into the full Schrödinger expression (1):

$$i\hbar \frac{\partial [\sum_i \psi_i \phi_i]}{\partial t} = \hat{H} \left[\sum_i \psi_i \phi_i \right]$$

Multiply by ϕ_j^* such that $\phi_j^* \phi_j = 1$.

$$i\hbar \frac{\partial \psi_j}{\partial t} = \sum_i \langle \phi_j | \hat{T}_N | \phi_i \rangle \psi_i + U_j \psi_j$$

$$i\hbar \frac{\partial \psi_j}{\partial t} = \sum_{i \neq j} \langle \phi_j | \hat{T}_N | \phi_i \rangle \psi_i + (\hat{T}_N + U_j) \psi_j$$

Define (as in equation (4.6))

$$\Lambda_{ji} = \delta_{ji} T_N - \langle \phi_j | T_N | \phi_i \rangle$$

and substitute into the previous equation to obtain equation (4.5):

$$i\hbar \frac{\partial \psi_j}{\partial t} = (T_N + U_j) \psi_j - \sum_i \Lambda_{ji} \psi_i$$

2. Derivation: This question examines in more detail the expression containing Λ_{ji} noting that $T_N = \frac{-\hbar^2}{2M} \nabla^2$

Substitution of this expression for T_N into equation (4.6) gives:

$$\Lambda_{ji}\psi_i = \frac{-\hbar^2}{2M} \delta_{ji} \nabla^2 \psi_i + \frac{\hbar^2}{2M} \langle \phi_j | \nabla^2 | \phi_i \rangle \psi_i \quad (2)$$

Applying the relationship for the second derivative of $\psi_i \phi_i$ given in the hint,

$$\nabla^2 \psi_i \phi_i = \phi_i \nabla^2 \psi_i + \psi_i \nabla^2 \phi_i + 2 \nabla \psi_i \nabla \phi_i$$

Substitute this into equation (2):

$$\langle \phi_j | \nabla^2 | \phi_i \rangle \psi_i = \langle \phi_j | \phi_i \rangle \nabla^2 \psi_i + \psi_i \langle \phi_j | \nabla^2 | \phi_i \rangle + 2 \langle \phi_j | \nabla | \phi_i \rangle \nabla \psi_i$$

and for $j \neq i$, because of the orthonormality condition for the electronic wavefunctions, $\langle \phi_j | \phi_i \rangle = 0$

$$\Lambda_{ji}\psi_i = \frac{\hbar^2}{2M} \psi_i \langle \phi_j | \nabla^2 | \phi_i \rangle + \frac{\hbar^2}{M} \langle \phi_j | \nabla | \phi_i \rangle \nabla \psi_i$$

We can therefore write

$$\Lambda_{ji} = \frac{\hbar^2}{2M} (2F_{ji}\nabla + G_{ji})$$

which is equation (4.8), with the definitions $F_{ji} = \langle \phi_j | \nabla | \phi_i \rangle$ and

$$G_{ji} = \langle \phi_j | \nabla^2 | \phi_i \rangle.$$

The expression for F_{ji} can be re-written by applying the gradient operator to both sides of the electronic Schrodinger equation $H_e \phi_i = U_i \phi_i$:

$$\nabla(H_e\phi_i) = H_e\nabla\phi_i + (\nabla H_e)\phi_i$$

$$\nabla(U_i\phi_i) = U_i\nabla\phi_i + (\nabla U_i)\phi_i$$

Setting the right hand sides of both equations to be equal, multiplying through by ϕ_j^* and integrating over electronic coordinates gives:

$$\langle\phi_j|\nabla U_i|\phi_i\rangle + U_i\langle\phi_j|\nabla|\phi_i\rangle = \langle\phi_j|H_e\nabla|\phi_i\rangle + \langle\phi_j|\nabla H_e|\phi_i\rangle \quad (3)$$

Each term can be evaluated as follows:

$$\langle\phi_j|\nabla|\phi_i\rangle = F_{ji} \text{ from the definition of } F_{ij}$$

$$\langle\phi_j|\nabla U_i|\phi_i\rangle = \nabla U_i\langle\phi_j|\phi_i\rangle = 0 \text{ for } i \neq j$$

$$\begin{aligned} \langle\phi_j|H_e\nabla|\phi_i\rangle &= \langle\phi_j|H_e|\nabla\phi_i\rangle = \langle\nabla\phi_i|H_e|\phi_j\rangle^* \\ &= \langle\nabla\phi_i|U_j|\phi_j\rangle^* = U_j\langle\nabla\phi_i|\phi_j\rangle^* = U_j\langle\phi_j|\nabla\phi_i\rangle = U_jF_{ji} \end{aligned}$$

Here, use has been made of the Hermiticity of H_e and the Schrodinger equation $H_e\phi_i = U_i\phi_i$. Equation (3) therefore becomes:

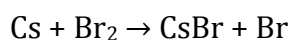
$$U_iF_{ji} = U_jF_{ji} + \langle\phi_j|\nabla H_e|\phi_i\rangle$$

This straightforwardly rearranges to

$$F_{ji} = \frac{\langle\phi_j|\nabla H_e|\phi_i\rangle}{U_i - U_j}$$

which is equation (4.9).

3. This is an example of a harpoon mechanism.



Sometimes the Born-Oppenheimer approximation is not valid, and it is not possible to separate nuclear and electronic motion. Therefore, we must allow for coupling between the nuclear and the electronic motions; this is possible by viewing the coupling as a perturbation to the decoupled Born-Oppenheimer motion.

In this reaction of Cs with Br₂, the neutral products are formed *via* a harpoon mechanism. This involves the jump of an electron (harpoon) from the Cs atom to the Br₂ molecule at large separations.

This electron transfers at the crossing radius, R_c . This occurs when:

$$V_{\text{covalent}}(R_c) = V_{\text{ionic}}(R_c)$$

i.e. at the intersection between the largely repulsive covalent PES, and the attractive ionic PES.

(The crossing between the ionic and covalent surfaces occurs when the electrostatic attraction between Cs⁺ and Br₂⁻ ions compensates for the energy required to form the ions from the neutral species):

$$V_{\text{ionic}} = 0 = \Delta E - \frac{e^2}{4\pi\epsilon_0 R_c}$$

$$\therefore R_c = \frac{e^2}{4\pi\epsilon_0 \Delta E} \quad (4)$$

$$\Delta E = I_{\text{Cs}} - EA_{\text{Br}}$$

$$= (3.89 - 2.55) \text{ eV}$$

$$= 1.34 \text{ eV} = 2.15 \times 10^{-19} \text{ J}$$

Inserting values for ϵ_0 , the vacuum permittivity, and e , the charge on an electron, and solving for R_c , *via* equation (4), yields:

$$R_c = 1.075 \times 10^{-9} \text{ m}$$

$$= 10.75 \text{ \AA}$$

$$\sigma = \int_0^{R_c} P(b) 2\pi b db = \pi R_c^2$$

$$\therefore \sigma = \pi \times 10.75^2 = 361.9 \text{ \AA}^2$$

4. Using the variation principle:

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}$$

$$\Psi = c_1\psi_1 + c_2\psi_2$$

$$\therefore \langle \Psi | \Psi \rangle = \langle c_1\psi_1 + c_2\psi_2 | c_1\psi_1 + c_2\psi_2 \rangle$$

$$\langle \Psi | \Psi \rangle = c_1^2 \langle \psi_1 | \psi_1 \rangle + c_2^2 \langle \psi_2 | \psi_2 \rangle + 2c_1c_2 \langle \psi_1 | \psi_2 \rangle$$

(since $\langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle$)

$$\langle \Psi | \Psi \rangle = c_1^2 + c_2^2 + 2c_1c_2 \langle \psi_1 | \psi_2 \rangle$$

Now, use the secular equations

$$\begin{pmatrix} H_{11} - E & H_{12} - ES \\ H_{21} - ES & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{vmatrix} H_{11} - E & H_{12} - ES \\ H_{21} - ES & H_{22} - E \end{vmatrix} = 0$$

$$H_{12} = H_{21}$$

When $S = 0$:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{vmatrix} = 0$$

$$(H_{11} - E)(H_{22} - E) - H_{12}^2 = 0$$

$$H_{11}H_{22} - H_{22}E - H_{11}E + E^2 - H_{12}^2 = 0$$

$$E^2 + E(-H_{11} - H_{22}) + (H_{11}H_{22} - H_{12}^2) = 0$$

Using the quadratic formula to find the roots of E :

$$E_{\pm} = \frac{H_{11} + H_{22} \pm \sqrt{(-H_{11} - H_{22})^2 - 4(H_{11}H_{22} - H_{12}^2)}}{2}$$

$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \frac{1}{2} [H_{11}^2 + H_{22}^2 + 2H_{11}H_{22} - 4H_{11}H_{22} + 4H_{12}^2]^{1/2}$$

$$E_{\pm} = \frac{H_{11} + H_{22}}{2} \pm \frac{1}{2} [(H_{11} - H_{22})^2 + 4H_{12}^2]^{1/2}$$

$$\langle \psi_1 | \hat{H} | \psi_2 \rangle = H_{12} = \Delta$$

$$\langle \psi_1 | \hat{H} | \psi_1 \rangle = H_{11} = \varepsilon_1$$

$$\langle \psi_2 | \hat{H} | \psi_2 \rangle = H_{22} = \varepsilon_2$$

$$\therefore E_{\pm} = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{1}{2} [(\varepsilon_1 - \varepsilon_2)^2 + 4\Delta^2]^{1/2} \quad (5)$$

5. $\varepsilon_1 = K(R - 4); \quad \varepsilon_2 = -K(R - 4); \quad \Delta = K/10$ (constant)

Substituting these values into equation (5):

$$E_{\pm} = \frac{K(R - 4) - K(R - 4)}{2} \pm \frac{1}{2} \left\{ [K(R - 4) + K(R - 4)]^2 + 4 \left(\frac{K}{10} \right)^2 \right\}^{1/2}$$

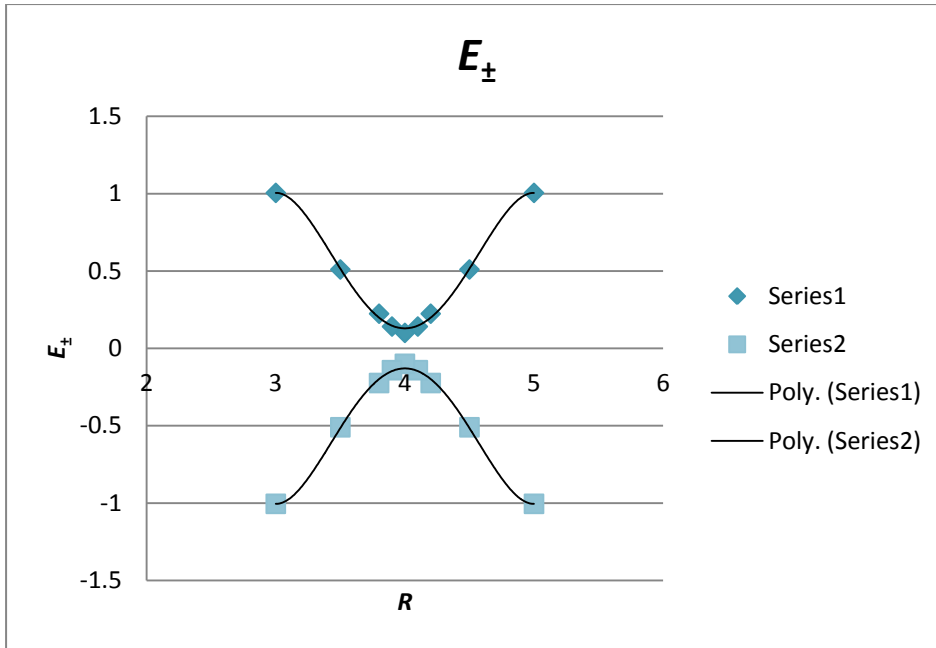
$$E_{\pm} = \pm \frac{1}{2} \left\{ [2K(R - 4)]^2 + \frac{4K^2}{100} \right\}^{1/2}$$

$$E_{\pm} = \pm \frac{1}{2} \left[4K^2(R - 4)^2 + \frac{4K^2}{100} \right]^{1/2}$$

$$E_{\pm} = \pm K \left[(R - 4)^2 + \frac{1}{100} \right]^{1/2}$$

R	E_{\pm}
5.0	$\pm 1.005K$
4.5	$\pm 0.510K$
4.2	$\pm 0.224K$
4.1	$\pm 0.141K$
4.0	$\pm 0.1K$
3.9	$\pm 0.141K$
3.8	$\pm 0.224K$
3.5	$\pm 0.510K$
3.0	$\pm 1.005K$

Plot a graph of these values with R on the x -axis, and E_{\pm} on the y -axis.



Next, determine the ratio $|c_1/c_2|$ as a function of R for each associated eigenfunction.

$$\begin{pmatrix} H_{11} - E & H_{12} \\ H_{12} & H_{22} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} \varepsilon_1 - E_{\pm} & \Delta \\ \Delta & \varepsilon_1 - E_{\pm} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$(\varepsilon_1 - E_{\pm})c_1 + \Delta c_2 = 0$$

$$(\varepsilon_1 - E_{\pm})c_1 = -\Delta c_2$$

$$\frac{c_1}{c_2} = -\frac{\Delta}{\varepsilon_1 - E_{\pm}}$$

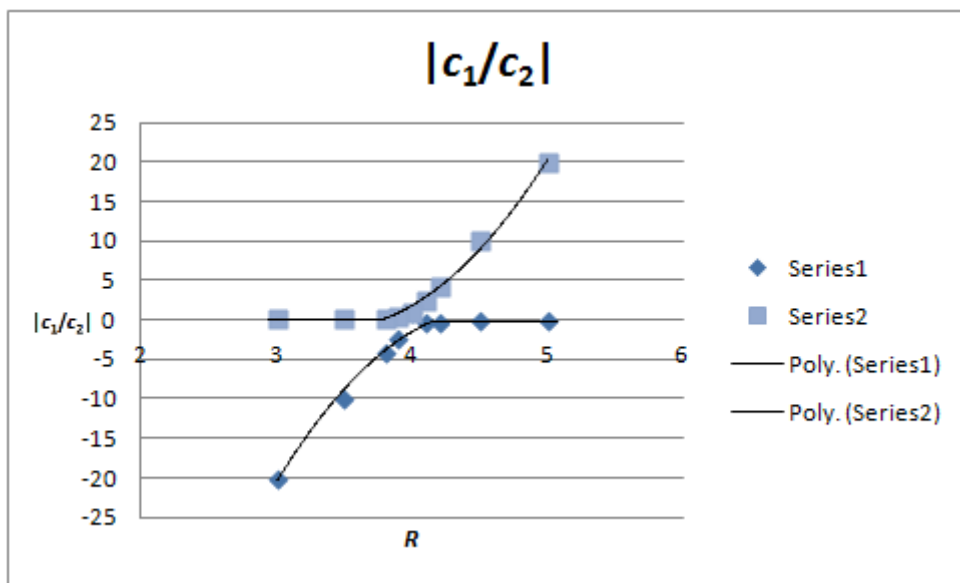
$$\frac{c_1}{c_2} = \frac{\Delta}{E_{\pm} - \varepsilon_1}$$

$$\frac{c_1}{c_2} = - \frac{K/10}{K(R-4) \pm K \left[(R-4)^2 + \frac{1}{100} \right]^{1/2}}$$

$$\frac{c_1}{c_2} = - \frac{1}{10 \left\{ (R-4) \pm \left[(R-4)^2 + \frac{1}{100} \right]^{1/2} \right\}}$$

R	$ c_1/c_2 $
5.0	-0.0499, +20.0499
4.5	-0.0990, +10.0990
4.2	-0.2361, +4.2361
4.1	-0.4142, +2.4142
4.0	± 1.0000
3.9	-2.4142, +0.4142
3.8	-4.2361, +0.2361
3.5	-10.0990, +0.0990
3.0	-20.0499, +0.0499

This plot shows that at large R , ψ_+ is dominated by c_1 , and ψ_- is dominated by c_2 .



6. The kinetic energy of the I and Br atoms at the crossing between the B and Y potentials is calculated from the difference between the photon energy and the potential energy:

$$KE = h\nu - hcE$$

with the factor of hc to convert E from units of cm^{-1} to J.

The reduced mass of IBr:

$$\mu = \frac{m_{\text{I}}m_{\text{Br}}}{m_{\text{I}} + m_{\text{Br}}}$$

$$\mu = \frac{126.9 \times 79.9}{126.9 + 79.9} u$$

$$\mu = 49.029 u = 8.144 \times 10^{-26} \text{ kg}$$

The relative speed of the I and Br atoms at the crossing point of the two PE curves is:

$$v = \sqrt{2KE/\mu}$$

These values and the parameters from the table can be inserted into equation (4.4).

For example, for a photon energy of 19000 cm^{-1} , $\nu = 992 \text{ m s}^{-1}$ and $P = 0.765$ is the probability of nonadiabatic dynamics (*i.e.* remaining on the diabatic B-state potential).

Thus, the probability of crossing from the diabatic B state to the Y state is $P_{\text{B/Y}} = 1 - P = 0.235$.

The other values plotted in figure 4.4 can be derived in a similar way.

N.B. the unit of \AA^{-1} must be converted to m^{-1} as part of the calculation.

7. For collinear reaction of $F(^2P_{3/2}) + H_2$ the total electronic angular momentum quantum number is $J = 3/2$ (the H_2 in its electronic ground state has no electronic angular momentum).

Allowed values of Ω correspond to the projections of J on the internuclear axis and are $\Omega = 3/2, 1/2$.

For the $HF(X^1\Sigma^+) + H(^2S_{1/2})$ products, $J' = 1/2$ and $\Omega' = 1/2$, with the ' denoting product quantum numbers.

For $HF(a^3\Pi) + H(^2S_{1/2})$ products, $\Omega'_{HF} = 0, 1$ and 2 and $\Omega'_H = 1/2$, giving possible values of $\Omega' = 1/2, 3/2$ and $5/2$.

The adiabatic correlations are thus:



in accord with figure 4.11.

Similar arguments give the correlations shown in figure 4.11 for the $F + D_2O \rightarrow DF + OD$ reaction (treating the reaction as collinear), with the additional complication that the ground electronic state of OD is a $^2\Pi$ state with $\Omega'_{OD} = 3/2$ and $1/2$.