Chapter 4 Problems

1. Starting from Eq. (4.1), derive Eq. (4.5). Make use of the expansion of the total wavefunction in nuclear (ψ) and electronic (ϕ) parts:

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

where explicit dependence on the coordinates R and r and on time has been dropped to simplify the notation. You will need to employ Eqs. (4.2), (4.3), and (4.6). *Hint:* the derivation starts by substituting the above expansion into Eq. (4.2), multiplication through by ϕ_j^* and integration over electronic coordinates, making use of the orthonormality of the electronic wavefunctions.

2. Starting from Eq. (4.6) and using the definition in Eq. (4.7) of the kinetic energy operator,

$$\hat{T}_N = -\frac{\hbar^2}{2M} \nabla^2$$

derive Eqs. (4.8) and (4.9) using the definitions $F_{ji} = \langle \phi_j | \nabla | \phi_i \rangle$ and $G_{ji} = \langle \phi_j | \nabla^2 | \phi_i \rangle$. *Hints:* to obtain Eq. (4.8), use the relationship for differentiation of the product of wavefunctions $\psi_i \phi_i$ that $\nabla^2 \psi_i \phi_i = \phi_i \nabla^2 \psi_i + \psi_i \nabla^2 \phi_i + 2\nabla \psi_i \nabla \phi_i$; the derivation of the second equality in Eq. (4.9) requires application of the gradient operator ∇ to both sides of the electronic Schrödinger Eq. (4.3).

3. The reaction $Cs + Br_2 \rightarrow CsBr + Br$ occurs *via* a harpoon mechanism in which an electron transfers from Cs to Br_2 at a distance R_c at which the covalent PES for the reaction is crossed by the ionic PES for $Cs^+ + Br_2^-$ ions. At large separations of the Cs and Br_2, the two PESs are separated by an energy corresponding to the difference between the ionization energy of the Cs atom ($I(Cs) = 3.89$ eV) and the electron affinity of the Br_2, ($EA(Br_2) = 2.55$ eV). Estimate a value for R_c assuming that the interaction energy between Cs and Br_2 on the covalent PES varies only

very weakly with separation at long range. Hence, estimate the cross section for this reaction.

4. Two diabatic states, characterized by the wavefunctions ψ_1 and ψ_2, arise as eigenfunctions of some simple approximate Hamiltonian for a diatomic molecule, and have energies ε_1 and ε_2, respectively. When the full Hamiltonian is considered, a small interaction $\langle \psi_1 | \hat{H} | \psi_2 \rangle = \Delta$ between these states occurs. By considering trial wavefunctions of the form $\Psi = c_1 \psi_1 + c_2 \psi_2$, and using the variational principle, find general expressions for the two lowest energy levels (see Study Box 4.1).

5. In the previous question, the energies ε_1 and ε_2 vary with internuclear separation R as $\varepsilon_1 = K(R - 4)$, $\varepsilon_2 = -K(R - 4)$, whereas $\Delta = K/10$ is a constant. Evaluate and plot the two lowest energy levels at $R = 4.0, 4.0 \pm 0.1, 4.0 \pm 0.2, 4.0 \pm 0.5$, and 4.0 ± 1.0. Plot also the ratio $|c_1/c_2|$ as a function of R for each associated eigenfunction. Comment on the results you obtain.

6. Use the Landau-Zener model (Eq. (4.11)) with the following parameters to calculate the transition probabilities from the B³Π(0⁺) to the Y³Σ⁻(0⁺) state of IBr at selected excitation photon energies in the range shown in Figure 4.4.

Parameters for the IBr B and Y states		
Energy at crossing (cm⁻¹)	V_{12} (cm⁻¹)	$\partial(V_2 - V_1/\partial R)$ (cm⁻¹ Å⁻¹)
16980	120	6424

7. For collinear approach of an F(²P) atom to an H₂ molecule, what are the allowed values of the Ω quantum number (for the projection of the total angular momentum on the internuclear axis)? What values of Ω arise for HF(X¹Σ⁺) + H and HF(a³Π) + H products? Using adiabatic correlation of Ω from reactants through to products, construct a correlation diagram for the adiabatic PESs for collinear reaction of F(²P) +H₂ → HF + H and compare your result to Figure 4.11.

Repeat the analysis for the reaction F $+D_2O \rightarrow DF +OD$ (with the approximation of a collinear reaction).