Problems and solutions for Chapter 5

P.\*A. Failure of the Born-Oppnehimer approximation. Let g and e denote the ground and excited electronic states. The Born-Oppnheimer separation fails when the matrix element  $\langle \psi_g(r;R) | T | \psi_e(r;R) \rangle$  is not negligible, where T is the kinetic energy operator for the nuclei. Take the case of a diatomic molecule, examine the commutator  $[H,\partial/\partial R]$  and hence show that

 $(E_g(R) - E_e(R))\langle \psi_g(r;R) | \partial / \partial R | \psi_e(r;R) \rangle = \langle \psi_g(r;R) | \partial H_{el} / \partial R | \psi_e(r;R) \rangle$ . The 'gap' between two different electronic states is  $(E_g(R) - E_e(R))$  and depends on the nuclear coordinate. Conclude that the Born-Oppneheimer approximation is most liable to fail when the gap is small.

S.A. In the Born-Oppenheimer separation, the electronic Schroedinger equation is to be solved for the nuclei fixed at a relative distance R. The distance R is then fixed at another value and the solution is repeated.By doing so for several values of R we obtain an electronic wave function and eigenvalue for each value of R. The ground and excited electronic state wave functions satisfy

$$H_{\rm el} \psi_{\rm g}(r, R) = E_{\rm g}(R) \psi_{\rm g}(r, R)$$
,  $H_{\rm el} \psi_{\rm e}(r, R) = E_{\rm e}(R) \psi_{\rm e}(r, R)$ 

 $H_{\rm el}$  is the electronic Hamiltonian, the sum of the kinetic energy operator for the motion of the electron and the different Coulombic terms, attraction between the electrons and the nuclei and repulsion between different electrons and between the two nuclei. Some of these potential energy terms depend on the internuclear distance *R*. The total Hamiltonian for a non-rotating is  $H = T + H_{\rm el}$  where  $T = -(\hbar^2/2\mu)\partial^2/\partial R^2$  is the kinetic energy operator for the relative motion of the nuclei. *T* commutes with the operator  $\partial/\partial R$  but

## MRD Problems and solutions for Chapter 5 page1

 $H_{\rm el}$  does not because of the potential energy terms that can depend on *R*. Evaluating the commutator by letting it act on some wave function  $\varphi(R)$ 

$$\left[H, \frac{\partial}{\partial R}\right] \varphi(R) = H \frac{\partial \varphi(R)}{\partial R} - \frac{\partial H \varphi(R)}{\partial R} = \frac{\partial H}{\partial R} \varphi(R)$$

Taking a matrix element of the commutator we can evaluate it either from the definition of the commutator or from its value. Since  $H_{el}$  is Hermitian and using the Dirac notation for integration over the coordinates only of the electrons

$$\begin{split} \left\langle \psi_{g}(r,R) \middle| \left[ H, \frac{\partial}{\partial R} \right] \middle| \psi_{e}(r,R) \right\rangle &= \left\langle \psi_{g}(r,R) \middle| H_{el} \frac{\partial}{\partial R} - \frac{\partial}{\partial R} H_{el} \middle| \psi_{e}(r,R) \right\rangle \\ &= \left( E_{g}(R) - E_{e}(R) \right) \left\langle \psi_{g}(r,R) \middle| \frac{\partial}{\partial R} \middle| \psi_{e}(r,R) \right\rangle \\ &= \left\langle \psi_{g}(r,R) \middle| \frac{\partial H_{el}}{\partial R} \middle| \psi_{e}(r,R) \right\rangle \end{split}$$

The derivative  $\partial H_{el}/\partial R$  of the electrostatic terms with respect *R* is a smooth function of *R* so the magnitude of the breakdown term  $\langle \psi_g(r,R) | \partial/\partial R | \psi_e(r,R) \rangle$  is determined by the energy gap  $(E_g(R) - E_e(R))$ . For those regions of *R* where the gap is small the Born-Oppenheimer approximation is more likely to fail. See sections 7.0.2 and 9.3.3 for more.

P.C. Qualitative considerations of energy disposal. The CO vibrational state distribution from the reaction of O + CN is found to be bimodal; there is significant population of quite high vibrational states, say v =10 up to the exoergicity limit but also lots of rather vibrationally cool molecules with a thermal like distribution. [J. Wolfrum, *Ber. Bunsenges. Phys. Chem.* **81**, 114 (1977)]. It is proposed that this highly exoergic reaction releases sufficient energy to form an N atom in the excited <sup>2</sup>D state. On the potential energy surface for the reaction leading to N\*, NCO is an intermediate. The reaction producing ground state N atoms is direct. Discuss the suggested explanation and propose one or more tests for it. (Hint: recall from figure 5.12 that we can measure the angular

MRD Problems and solutions for Chapter 5 page2

distribution for different internal states of the products). In a further experiment the reaction was initiated with vibrationally hot CN. How will the CO vibrational distribution change ?

S.C. There are two products channels for this highly exoergic reaction

$$O(^{3}P)+CN \rightarrow \begin{cases} CO+N(^{4}S) \\ CO+N(^{2}D) \end{cases}$$

The channel forming ground state N atoms is direct and exoergic and produces vibrationally hot CO. The channel forming electronically excited  $N(^2D)$  atoms is necessarily less exoergic and it also proceeds over a well corresponding to the NCO intermediate. This channel produces vibrationally colder CO. The sprinkler model, section 4.4.1, suggests that the angular distribution of the products of this channel will have a forward backwards symmetry. If the reactant CN is vibrationally excited this will not have a special dynamical role for the reaction proceeding over a well because while the system samples the well the available energy will be redistributed over all modes.

P.\*E. Mass scaled coordinates. Statics. Using appendix 5.B, scale the potential surface or problem D for the case when (a) The attacking atom is light/heavy compared to the two others, (b) Atom B is by far heavier than the two others, (c) All three masses are equal.

S.E. Figure B5.2 shows the two skewed mass scaled axes stretched by a and b respectively where  $a^2 = \mu_{A-BC} = m_A m_{BC} / (m_A + m_{BC})$  is the reduced mass in the reactants channel and  $b^2 = \mu_{AB-C} = m_{AB}m_C / (m_{AB} + m_C)$  is the reduced mass in the products channel. (a). If the attacking atom is of low mass, L+HH or  $m_A < m_{BC}$  then a < b and vice versa if it is heavier. (b). If the exchange atom B is heavier a is comparable to b but the skewing angle is low because  $\cos \beta \rightarrow 1$ . (c). When all three atoms are of equal

MRD Problems and solutions for Chapter 5 page3

mass the skewing angle is 60°. (d). When the mass of all atoms is increased by the same factor the skewed potential looks exactly the same, only the ticks along the distance axes change by the square root of this factor. What this means is that the trajectory will look exactly the same and the only difference is that the time runs faster by by the square root of this factor.

P.\*G. The Evans-Polanyi model. Go to the classic text Glasstone, Laidler et al. (1941) and see the derivation that leads to the diabatic potentials for the reactants. In the notation of section 5.1.3, this diabatic surface has the functional form

$$V_{A+BC} = Q_{AB} + Q_{BC} + Q_{CA} + \left[J_{BC} - \frac{1}{2}(J_{AB} + J_{AC})\right]$$
.

(a) Write, by symmetry, the diabatic potential that correlates to the products. (b) Draw the two diabatic potentials for a collinear collision, for a very exoergic, a mildly exoergic and a thermoneutral reaction. You will need to infer the J and Q terms as discussed in the text. The drawing can be done using even a hand-held graphic calculator but is best done on a computer using a graphic program. (c) Infer the Hammond postulate from your work in (b). (d) Get another result: the height of the barrier to reaction correlates with the exoergicity.

S.G. By symmetry

$$V_{\rm AB+C} = Q_{\rm AB} + Q_{\rm BC} + Q_{\rm AC} + \left[J_{\rm AB} - \frac{1}{2}(J_{\rm BC} + J_{\rm AC})\right]$$

(c) and (d): See figure 11.21.

P.\*I. Chaos results in a rapid erasure of details of the starting point. We consider a very simple example and for brevity do not discuss the kinetic context in which this example arises. Let  $\theta$  be an angle, measured in units of  $2\pi$ . Say we write  $\theta$  in a binary notation.

MRD Problems and solutions for Chapter 5 page4

Then trigonometric functions depend only on the fractional part of  $\theta$ . Let successive values of  $\theta$  be generated by the rule  $\theta_{n+1} = 2\theta_n$ . Imagine implementing this iteration on a computer. Let  $\theta_0$  be the initial value. On a computer  $\theta_0$  is specified as a sequence of digits of finite length, say 16 figures. Show that with each iteration you lose one digit in accuracy,  $\theta_1$  is known only to 15 digits,  $\theta_2$  is known only to 14 digits, etc. Implication: an expression can be mathematically an identity and yet, when implemented on a digital computer, it can rapidly lose numerical accuracy.

S.I. The equation giving rise to this problem is the iteration process

$$x_{n+1} = 4x_n(1-x_n)$$

To examine the solution, put  $x_n = \sin^2 \theta_n$  then we recover the mapping as given in the text,  $\theta_{n+1} = 2\theta_n$ . We take the angle to be measured in units of  $2\pi$  which because of the periodicity of the trig functions implies that the integer part of the angle does not matter in determining *x*. We represent the angle as a binary number and start from the initial value  $\theta_0 = 0.10101100$  meaning that we keep eight significant digits. Modulo  $2\pi$  we have  $\theta_1 = 2\theta_0 = 0.0101100$  which represents a loss of one significant figure. Modulo  $2\pi$  we next have  $\theta_2 = 2\theta_1 = 0.101100$  and then  $\theta_3 = 2\theta_2 = 0.01100$ . By n = 8 the value of  $\theta$  is completely indeterminate. It is possible to keep more significant digits in the initial value  $\theta_0$  but however many digits we keep there will come a step *n* beyond which all accuracy is lost.

P.K. Limitations on the Monte Carlo sampling of initial conditions. Say you want to compute the reaction rate constant when there is a rather small steric factor or/and a rather high activation energy. (a) Will you use a Monte Carlo sampling of initial conditions? Discuss in detail why we think that getting an accurate result will require a

MRD Problems and solutions for Chapter 5 page5

considerable consumption of computer time. (b) Can you try to suggest at least two different options for getting the result while computing far fewer trajectories? For a quick start see R. L. Jaffe, J. M. Henry and J. B. Anderson, *J. Chem. Phys.* **59**, 1128 (1973).

S.K. (a). If the dynamics of the reaction are such that out of many possible initial conditions only a few lead to reaction then the number of reactive trajectories is quite small compared to the total number of trajectories that arte computed  $N_{\rm R} \ll N$ . But, see the discussion of equation (5A.7), the fractional error scales as  $1/\sqrt{N_{\rm R}}$ . So to get reasonable confidence in the result we need to run many more trajectories than otherwise. (b). Running many trajectories is a waste because under the stated circumstances most of the trajectories will be non reactive. To reduce waste we need to bias the selection of which trajectories to generate. This is sometimes called importance sampling because only the important initial conditions are sampled. For example, if only nearly collinear collisions lead to reaction we can sample only  $-0.9 \ge \cos \gamma \ge -1$  and for lower angles of attack take the reaction probability to be zero.

P.M. Reactions with a negative activation energy. Reactions that proceed via formation of a complex and are measured at higher pressures can show a negative activation energy. As an example consider the reaction of  $C_2H_5$  with  $O_2$  as shown in figure 5.6. The first step is the formation of the  $C_2H_5$ · $O_2$  complex. At higher pressure this complex is stabilized by collisions and is brought to thermal equilibrium with the reactants. The rate determining step is the isomerization of the complex to to  $CH_2=CH_2$ · $O_2H$  as shown in the concerted elimination pathway. (a) Examine figure 5.6 and explain why the rate of the net chemical change can manifest a negative activation energy. The measured (O. Dobis and S. W. Benson, JACS, 115, 8798 (1993)) high pressure value is about -20 kJmol<sup>-1</sup>. (b) Suggest why the Arrhenius A factor for the barrier crossing isomerization will be low. (c)

MRD Problems and solutions for Chapter 5 page6

The reaction can also proceed by a direct route as shown in figure 5.6. Discuss if this route is favored at low or at high temperatures.

S.M. (a). The kinetic scheme at high pressure is

$$A+B \rightleftharpoons M$$
,  $M \xrightarrow{k} N$ 

The rate of formation of N can then be written as

$$\frac{d}{dt}[\mathbf{N}] = k[\mathbf{M}] = kK[\mathbf{A}][\mathbf{B}] \quad , \quad K = \frac{[\mathbf{M}]}{[\mathbf{A}][\mathbf{B}]}$$

The second order rate constant is then kK where k is a usual rate constant for barrier crossing and as such will generally increase with increasing temperature meaning that it has a positive activation energy. But K is an equilibrium constant for a reaction where the product, M thermalized, is much lower in energy than the reactants. K is thus expected to strongly decrease with increasing temperature. Very crudely, K will decrease as  $\exp(-\Delta E_0 / k_B T)$  where  $\Delta E_0$  is the (large negative) exoergicity of the A+B reaction to form M. Similarly, k will increase as  $\exp(-E_a / k_B T)$  where, roughly,  $E_a$  is the barrier from M to N. Inspection of figure 5.6 shows that this barrier can be smaller than  $-\Delta E_0$ .

(b). The isomerization likely requires ring formation so as to shift the H atom between the two ends of the molecule. The likelihood of the two ends meeting is low meaning that the formation of the transition state is improbable or, in other words, the entropy of activation is quite negative.

(c). The direct route is over a (small) barrier and so will have a positive activation energy. The route via the well has a negative activation energy. The direct route will be favored at higher temperatures.