Problems and solutions for Chapter 4

P.A. How large is the angular momentum in molecular collisions? The angular momentum L has the same dimensions, length·momentum, as Planck's constant. The quantum number l is a measure of L in units of $\hbar$, $L = l\hbar$. Classically, $L = \mu v b = \hbar k b$ where k is the wave number, $k = \mu v / \hbar$. For molecular collisions the reduced mass μ can vary by over two orders of magnitude but even for H + H collision it is three orders of magnitude bigger than the mass of the electron. For reasonable values of the impact parameter and collision velocity and remembering that for reactions with a barrier we need that $E_T = \mu v^2 / 2 > E_0$, compute a reasonable range for L values. Conclude that typically $l >> 1$ and that it requires very low velocities to be in the fully quantal regime where only a few values of l are important. The dimensionless parameter $A = k\sigma$ where σ is the range parameter of the potential is a useful guide to the range of l values that contribute.

S.A. $L = \mu v b$ where μ is the reduced mass and v is the velocity of the relative motion. For H+H collision μ = 1/2 atomic mass units. To compute in atomic units (au) recall that 1 au of mass is the mass of an electron so 1 amu ≅ 1830 au of mass. A reasonable range for the impact parameter for the H+H collision is few au of length. The au of velocity is the velocity of the electron in the first Bohr orbit, $e^2/\hbar = 2.19 \cdot 10^8$ cm / sec. At room temperature a velocity of somewhat over 10^5 cm / sec is reasonable for an H atom. So L is of the order of ten atomic units or, since in au $\hbar = 1$, for the H+H collision at low velocity we have $L \approx 10\hbar$. At a similar velocity the K+I_2 collision as shown in figure 4.12 the reduced mass is a factor of about 80 higher and the range of impact parameters is also about a factor of ten higher, recall the harpoon mechanism. So now L is several thousand $\hbar$ units.

P.C. The relative position vector of two particles is $\mathbf{R}=\mathbf{R}_1-\mathbf{R}_2$. Assume that the potential between them depends only on the distance R. Derive equation (4.1) by writing equations of motion for $\mathbf{R}_1$ and $\mathbf{R}_2$.

S.C.

$$\mathbf{R}=\mathbf{R}_1-\mathbf{R}_2 \quad , \quad m_1\frac{d^2\mathbf{R}_1}{dt^2}=-\hat{\mathbf{R}}\frac{\partial V(R)}{\partial R}\frac{\partial R}{\partial R_1} \quad , \quad m_2\frac{d\mathbf{R}_2}{dt}=-(-\hat{\mathbf{R}})\frac{\partial V(R)}{\partial R}\frac{\partial R}{\partial R_2}$$

$$\frac{d^2\mathbf{R}}{dt^2}=-\hat{\mathbf{R}}\frac{\partial V(R)}{\partial R}\left(\frac{\partial R}{m_1\partial R_1}+\frac{\partial R}{m_2\partial R_2}\right)=-\mu^{-1}\hat{\mathbf{R}}\frac{\partial V(R)}{\partial R} \quad , \quad \mu^{-1}=\left(\frac{1}{m_1}+\frac{1}{m_2}\right)$$

P.E. Direct chemical reactions are fast. Suppose the two reactants approach one another and suddenly switch into products that then depart. By analogy with the scattering amplitude for elastic collisions, equation (4.36), we can now write the amplitude for reaction as $\exp(i\delta_{out})|S_l|\exp(i\delta_{in})$ where $P(b)=|S_l|^2$. Show that this amplitude accounts not only for the deflection angle having the form in the text but also that there is no time delay due to the reaction itself. The delay is entirely made up from any excess time it takes the reactants to move in and similarly for the products to receded from one another.

S.E. The deflection angle along the trajectory is, cf. Equation (4.39),

$$\theta=\frac{\partial}{\partial l}\begin{pmatrix}\text{phase shift acquired during the}\\ \text{motion up to the turning point}\end{pmatrix}+\frac{\partial}{\partial l}\begin{pmatrix}\text{phase shift acquired during the}\\ \text{motion from the turning point out}\end{pmatrix}$$

For an elastic collision the two motions have the same phase shift hence Equation (4.39). For the model of a sudden direct reaction the phase shifts on the way in and out can be different. If we make the further approximation that the motion in and out is that of hard spheres we get the special case of equation (4.50).

P.G. The $K+(CN)_2$ and $K+CH_3CN$ reactions. In many ways the CN radical acts as a halogen atom, Bersohn (1976) . Compare and contrast the two KCN forming reactions. Chapter 5 will allow you to draw conclusions regarding the vibrational excitation of the nascent KCN. Another similarity is the stereochemistry, with KCN being formed preferentially for a K approach from the CN end of the CH_3CN molecule, see figure 1.5. A collision of fast (hyperthermal) K atoms with CH_3CN molecules leads to the formation of separated ions K^+ and CN^-. The CN^- ions are produced predominantly by attack of the K atom on the CH_3-end of CH_3CN, [S. A. Harris, P. W. Harland, and P. R. Brooks, *Phys. Chem. Chem. Phys.* **2**, 787 (2000)]. The electron apparently enters the lowest unfilled π^*CN orbital to form an unstable linear molecular negative ion that then breaks up as it attempts to bend into the geometry of the stable products, KCN and CH_3.

S.G. If we regard CN as a halogen 'atom' then the $K+(CN)_2$ and $K+CH_3CN$ reactions are the analogues of the $K+I_2$ and the $K+CH_3I$ reactions contrasted in figures 4.12 and 4.14. The exoergic harpoon reaction $K+(CN)_2$ produces vibrationally excited KCN because it is an early downhill reaction, as discussed in chapter 5.