Chapter 12 Problems

1. (a) A simple classical one-dimensional model for the collision energy dependence of the cross section of a chemical reaction uses the following expression

$$E_{\mathrm{t}} = \frac{1}{2}\mu\dot{\boldsymbol{R}}^2 + V_{\mathrm{eff}}(R),$$

where E_{t} is the initial collision energy, and $V_{\mathrm{eff}}(R)$ is the radial dependence of the effective potential. Explain the origins of this expression, and present arguments to show that the effective potential may be written

$$V_{\mathrm{eff}}(R) = V(R) + E_{\mathrm{t}}\frac{b^2}{R^2}, \tag{12.213}$$

where $V(R)$ is the radial dependence of the potential energy, and b is the impact parameter for the collision. Recall that the kinetic energy associated with orbital motion can be written $E_{\mathrm{cent}} = |\ell|^2/2\mu R^2$.

(b) For a reaction between an ion and a molecule, the long range ion-induced dipole interaction potential has the form

$$V(R) = -\frac{C_4}{R^4},$$

where the coefficient is defined $C_4 = \alpha' e^2/(8\pi\varepsilon_0)$, and the constant α' is polarizability volume of the molecule. Use this expression, together with equation (12.213) above, to show that the location of the maximum in the centrifugal barrier on the effective potential is given by the expression

$$R_0 = \left(\frac{2C_4}{E_{\mathrm{t}}b^2}\right)^{1/2}$$

(c) Hence show that, for the radial kinetic energy at the barrier to be greater than zero, the impact parameter for the ion-molecule reaction is limited by the equation

$$b^2 \leq \left(\frac{4C_4}{E_t}\right)^{1/2}$$

Use this expression to estimate the cross section for the reaction (known as the capture cross section), stating any additional assumptions made, and sketch the dependence of the cross section on collision energy (*i.e.* the excitation function).

(d) The polarisability volume, α', of O_2 is 1.4×10^{-30} m^3. Estimate the ion-induced dipole contribution to the capture cross section for the $Ca^+ + O_2$ reaction. Employ a mean collision energy corresponding to a temperature of 10 K.

2. The *K*-matrix boundary conditions for an *s*-wave are given in Eq. (12.113),

$$u_0^{(K)}(r) = \sin kr - K \cos kr \qquad (12.214)$$

The *S*-matrix boundary conditions for this wavefunction are

$$u_0^{(S)}(r) = -e^{-ikr} + e^{ikr}S \qquad (12.215)$$

The difference between these boundary conditions is only the normalization of the wavefunction, *i.e.*

$$u_0^{(K)}(r) = Au_0^{(S)}(r), \qquad (12.216)$$

where *A* is a constant. Derive the relation between the *S*- and the *K*-matrix [Eq. (12.117)].
Hint: take the derivative with respect to *r* of the last equation:

$$\frac{\mathrm{d}}{\mathrm{d}r}u_0^{(K)}(r) = A\frac{\mathrm{d}}{\mathrm{d}r}u_0^{(S)}(r) \qquad (12.217)$$

Assume *K* to be known. For some fixed value or *r* Eqs. (12.216) and (12.217) are now two equations linear in *A* and *S*, so they can be solved to find *S*.