PROBLEMS

Chem 163A

23. The Morse potential is a moderately realistic potential describing molecular vibration

$$U(x) = D_e(1 - e^{-\beta x})^2$$

where $x = x_2 - x_1 - r_e$.

(a) What is U(x) when the atoms are at the equilibrium internuclear separation?

(b) What is U(x) as $x \rightarrow \infty$?

(c) Expand U(x) in a Taylor series around $(x_2 - x_1) = r_e$ [i.e., x = 0] to obtain

$$U(x) = D_e\beta^2x^2 - D_e\,\beta^3x^3 + \ldots$$

(d) In terms of the parameters of the Morse potential, what is the force constant k for the harmonic approximation? Given that $D_e = 7.31 \times 10^{-19}$ J molecule^{-1} and $\beta = 1.82 \times 10^{10}$ m^{-1} for HCl, calculate k for HCl.

24. Classically angular momentum is given by $\vec{\ell} = \vec{r} \times \vec{p}$, and thus the quantum mechanical operator is $\hat{\vec{\ell}}_{op} = \hat{\vec{r}}_{op} \times \hat{\vec{p}}_{op}$. $\hat{\vec{\ell}}_{op}$ can be written as a determinant (see McQ, prob. 4-4, p. 143):

$$\hat{\vec{\ell}}_{op} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ \frac{\hbar}{i}\frac{\partial}{\partial x} & \frac{\hbar}{i}\frac{\partial}{\partial y} & \frac{\hbar}{i}\frac{\partial}{\partial z} \end{vmatrix}$$

(a) Write the operators for the components $\hat{\ell}_x$, $\hat{\ell}_y$ and $\hat{\ell}_z$.

*(b) Do $\hat{\ell}_z$ and $\hat{\ell}_y$ commute? What is $\left[\hat{\ell}_z, \hat{\ell}_y\right] = ?$

25. Evaluate the following integrals in spherical polar coordinates:

(a) $\int_0^R dr \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \; r^2 \sin\theta$

(b) $\int (e^{-\alpha r})^2 d\tau$

26. Show that the spherical harmonic

$$Y_2^0(\theta, \phi) = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

is an eigenfunction of the rigid rotor hamiltonian

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \; \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \; \frac{\partial^2}{\partial\phi^2}\right]$$

and determine its eigenvalue.

27. MacQ. #6-13.