Student Name, Number & Section Key

Chemistry 483

Practice Second Examination

11 October 2009

1. (40 points) Define and/or characterize

a) Secular Determinant

The determinant that determines the energy in a linear variation problem.

b) Trial function

The function used in the variation method to estimate the energy of a system.

c) Rigid Rotor

A model for the rotational motion of a diatomic molecule in which the distance between the two nuclei is fixed.

d) Hamiltonian for He

$$\hat{\mathcal{H}} = \hat{H}(1) + \hat{H}(2) + \frac{1}{r_{12}}$$

where $\hat{H}(j) = -\frac{1}{2}\nabla_j^2 - \frac{2}{r_j}$

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e) Morse Potential

$$V(x) = D(1 - e^{-\beta x})^2$$

where $x = R - R_0$ & β is a parameter
D is the dissociation energy & R_0 is the equilibrium bond length

f) Radial Distribution Function

$r^2 R_{N\ell}^2(r)$; measures the probability of finding an electron on the surface of a sphere of radius r

g) Force constant

$k = \left.\frac{d^2V}{dx^2}\right)_{x=0}$: the second derivative of the potential energy function evaluated at the equilibrium bond length

h) Parity

if the function $f(-x) = -f(x)$ it has odd parity. If $f(x) = f(-x)$ it has even parity

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2. (15 points) Show that the most probable value of r in the1s state of H is a_0

$$\psi_{1s} = R_{1s}(r)\, Y_0^0$$

$$R_{1s}(r) = \frac{2}{\sqrt{a_0^3}}\, e^{-r/a_0}$$

radial distribution function $= f = r^2 R_{1s}^2$

$$\frac{df}{dr} = r^2\, 2R_{1s}\frac{dR_{1s}}{dr} + 2rR_{1s}^2 = 0$$

$$r\frac{dR_{1s}}{dr} + R_{1s} = 0$$

$$-\frac{r}{a_0} + 1 = 0 \quad \therefore \quad r = a_0$$

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3. (15 points)

If one selects $\psi = e^{-\alpha r^2}$ as the trial function for the H atom and applies the variation method one finds the energy (in atomic units) has the form

$$E(\alpha) = \frac{3\alpha}{2} - Z\sqrt{\frac{8\alpha}{\pi}}$$

Determine the optimal value of α and the associated energy. Compare with the exact energy.

$$\frac{dE}{d\alpha} = \frac{3}{2} - Z\sqrt{\frac{8}{\pi}}\,\frac{1}{2}\,\alpha^{-1/2} = 0$$

$$\sqrt{\alpha}\,3 = Z\sqrt{\frac{8}{\pi}}$$

$$\sqrt{\alpha} = Z\sqrt{\frac{8}{9\pi}}$$

$$\alpha_{opt} = Z^2\frac{8}{9\pi}$$

Exact (in atomic units) $= \boxed{-\frac{1}{2}Z^2}$

$\therefore$ compare

$$E(\alpha_{opt}) = \frac{3}{2}\,\frac{8}{9\pi}Z^2 - Z^2\sqrt{\frac{8}{\pi}}\sqrt{\frac{8}{9\pi}} = -\frac{4Z^2}{3\pi} = \boxed{-0.4244Z^2}$$

So one gets ~85% of the energy

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4. (15 points) Use perturbation theory and calculate the first order correction to the energy of the ground state of a harmonic oscillator when it is subjected to the perturbation

$$V_{pert} = \frac{\gamma}{6} x^3$$

Recall that $$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2}$$

$\hat{\mathcal{H}} = \hat{\mathcal{H}}^\circ + V_{pert}$

$E_{pert} = \langle \psi_0 | V_{pert} | \psi_0 \rangle = 0$ by symmetry

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5. (15 points) The force constant of $^{79}Br^{79}Br$ is 240 Nm^{-1}. Calculate the fundamental vibrational frequency and the zero-point energy of $^{79}Br^{79}Br$.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{M^2}{2M} = \frac{M}{2}$$

$$\mu = \frac{M}{2} = \frac{(79)(1.6605 \times 10^{-27}\ kg)}{2} = 65.590 \times 10^{-27}$$

$$\sqrt{\frac{k}{\mu}} = \sqrt{\frac{240 \times 10^{27}}{65.590}} = \sqrt{36.59 \times 10^{26}}$$

$$= 6.05 \times 10^{13}$$

$$\nu = \frac{6.05 \times 10^{13}}{2\pi} = 0.963 \times 10^{13}\ sec^{-1}$$

$$\text{zero point energy} = \frac{h\nu}{2} = \frac{(6.626 \times 10^{-34})(0.963 \times 10^{13})}{2}$$

$$ZPE = 3.19 \times 10^{-21}\ J$$

note $$\tilde{\nu} = \frac{\nu}{c} = \frac{0.963 \times 10^{13}\ sec^{-1}}{3 \times 10^{10}\ \frac{cm}{sec}} = 321\ cm^{-1}$$