Chem 1410 | Exam 2

Name: Date:

1. (15 pts) Consider the 1s3d configuration of the He atom.

   a) What are the term symbols of the possible states?

   $^1D, {}^3D$

   b) Which of these states is expected to be the lowest in energy?

   ^3D

   c) If you shine light on the He in the lowest energy state derived from the 1s3d configuration to what states would there be dipole allowed transitions?

   $^3D \rightarrow {}^3P$ or ^3F

2. (15 pts) What electronic states are possible for the $1\sigma_g 1\sigma_u$ configuration of H2.

   $^3\Sigma_u, {}^1\Sigma_u$

3. (25 pts) Consider the particle (an electron) in the box problem with a sloped bottom, i.e.,

   $V = \infty, \; x < 0$

   $V = \left(x - a/2\right), \; 0 \le x \le a$

   $V = \infty, \; x > a$

   Choose as $H^{(0)}$ the Hamiltonian for the system with an unsloped potential. What is the energy of ground state of this system to 0th, 1st, and 2nd order perturbation theory? If more than one excited state appears in the sum over states, use only the lowest excited state that the perturbation mixes ground state.

3. $\langle 0|V|0\rangle = 0$

$$E^{(2)} = \frac{|\langle 0|V|1\rangle|^2}{E_0 - E_1} = \frac{\left[\frac{2}{a}\int_0^a \left(x-\frac{a}{2}\right)\sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx\right]^2}{-\frac{3\pi^2}{2a^2}}$$

$$= \frac{-\frac{4}{a^2}\left(\frac{8a^2}{9\pi^2}\right)^2}{\frac{3\pi^2}{2a^2}} = -\frac{8}{3\pi^2}\,\frac{64a^4}{81\pi^4} = -\frac{512a^4}{243\pi^6}$$

4. $\psi_1 = c\sin(kx)$, $\psi_2 = c\sin k(x-3)$

$\psi_1(2) = 0 = c\sin 2k \Rightarrow 2k = \pi$, $k = \pi/2$

$\psi_2(1) = 0 = c\sin k(-2) \Rightarrow -2k = \pi$ $k = -\pi/2$

$\psi_1 = c\sin\left(\frac{\pi x}{2}\right)$, $\psi_2 = c\sin\left(-\frac{\pi}{2}(x-3)\right)$

$$E = \frac{\int_0^2 \sin\left(\frac{\pi x}{2}\right)H\sin\left(\frac{\pi x}{2}\right)dx + \int_1^3 \sin\left(\frac{\pi}{2}(3-x)\right)H\sin\left(\frac{\pi}{2}(3-x)\right)dx + 2\int_1^2 \sin\left(\frac{\pi x}{2}\right)H\sin\left(\frac{\pi}{2}(3-x)\right)dx}{\langle\psi|\psi\rangle}$$

the 1st and 2nd integrals have only KE contributions

the third integral has both KE and PE contributions.

5. The spacing between consecutive levels is $2\tilde{B}e$

So $\tilde{B}e \sim 10.4\ cm^{-1}$.

$$\tilde{B}e = \frac{h}{8\pi^2\mu r^2 c}$$

Solve for r, get $r = 1.27\ \text{Å}$