Chemistry 332 **Problem Set #2** (due Tuesday 31 January, in class)

1. A ground-state electron is in a one-dimensional box between $x = -L/2$ and $x = L/2$. If the potential energy i the box is zero, the wave function and the energy of the electron are

[4] $\psi_1(x) = (2/L)^{1/2}\cos(\pi x/2L)$ $E_1 = h^2/8mL^2$

Suppose the linear electric potential $\varphi(x) = bx$ is applied to the box. (b is a constant.) Use perturbation thec to estimate ΔE, the first-order correction to the energy. *Hint*: $\hat{H}^{(1)} = -e\varphi(x)$

2. **a)** The trial wave function with adjustable parameter Z'

$$\chi(r_1, r_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} \exp(-Z'r_1/a_0)\frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a_0}\right)^{3/2} \exp(-Z'r_2/a_0)$$

[5] gives

$$E' = \left[(Z')^2 - \frac{11}{8}Z'\right]\frac{e^2}{4\pi\varepsilon_0 a_0}$$

for the energy of the hydride ion (H^-). Calculate the optimal values of Z' and E'. Based on screening effect is the value of Z' physically reasonable?

b) Based on **a**, is H^- likely to exist as a stable chemical species? Discuss briefly. *Hint*. Consider the energetics of ground-state hydrogen atom ($E_1 = -13.60$ eV) reacting with an electron: $e^- + H = H^-$.

3. Classify each of the following functions as symmetric, antisymmetric or neither.

[6]

a) $f(1)\, g(2)\, \alpha(1)\, \alpha(2)$

b) $f(1) f(2)\, [\alpha(1)\, \beta(2) - \alpha(2)\, \beta(1)]$

c) $f(1) f(2) f(3)\, \alpha(1)\, \alpha(2)\, \alpha(3)$

d) $\exp[-a(r_1 - r_2)]$

e) $[f(1)\, g(2) - f(2)\, g(1)][\alpha(1)\, \beta(2) - \alpha(2)\, \beta(1)]$

f) $\exp[-a(r_1 - r_2)^2]$

4. Does a non-trival solution exist for the following set of homogenous equations? Justify your answer.

[2]

$$3c_1 + 4c_2 + c_3 = 0$$

$$c_1 + 3c_2 - 2c_3 = 0$$

$$c_1 - 2c_2 + 4c_3 = 0$$

Chem 332 **Assignment #2**

Q1 An electron in a one-dimensional box ($-L/2 < x < L/2$) of width L

$$\psi^{(0)} = \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{2L}\right) \qquad E_1 = \frac{h^2}{8mL^2}$$

exact "zero-order" (no perturbation) wave function and energy

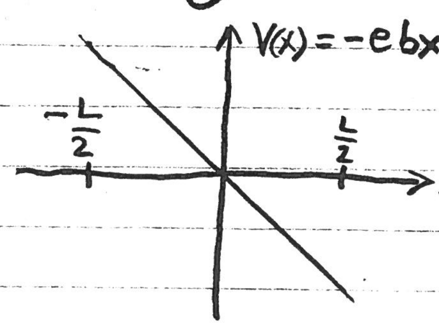
Perturbation: electric field $\varphi(x) = bx$ is applied, giving the electron the additional electric potential energy $-e\varphi(x) = -ebx$ ($-e$ = electron charge)

1st-order correction to the energy:

$$\Delta E^{(1)} = \int_{-\frac{L}{2}}^{L/2} \psi^{(0)*} \hat{H}_1 \psi^{(0)} dx$$

$$= \int_{-L/2}^{L/2} \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{2L}\right) (-ebx) \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{2L}\right) dx$$

$$= -\frac{2eb}{L} \int_{-L/2}^{L/2} \underbrace{x}_{\text{odd}} \ \underbrace{\cos^2\left(\frac{\pi x}{2L}\right)}_{\text{even}} dx = 0$$



makes sense!
extra potential energy for $x > 0$
cancelled by negative pot. energy for $x < 0$

Q2 a) Predicted energy of the H^- anion for "screened" nuclear charge Z':

$$E' = \left[(Z')^2 - \frac{11}{8}Z'\right]\frac{e^2}{4\pi\varepsilon_0 a_0}$$

The "best" (optimal) value of Z' is calculated by minimizing E', bring the predicted energy to a minimum, as close as possible to the true energy.

constants

$$\frac{dE'}{dZ'} = 0 = \frac{e^2}{4\pi\varepsilon_0 a_0}\frac{d}{dZ'}\left[(Z')^2 - \frac{11}{8}Z'\right]$$

$$0 = \frac{d}{dZ'}\left[(Z')^2 - \frac{11}{8}Z'\right] = 2Z' - \frac{11}{8}$$

$$Z' = \frac{11}{16} = 0.6875 \text{ (optimal } Z' \text{ value)}$$

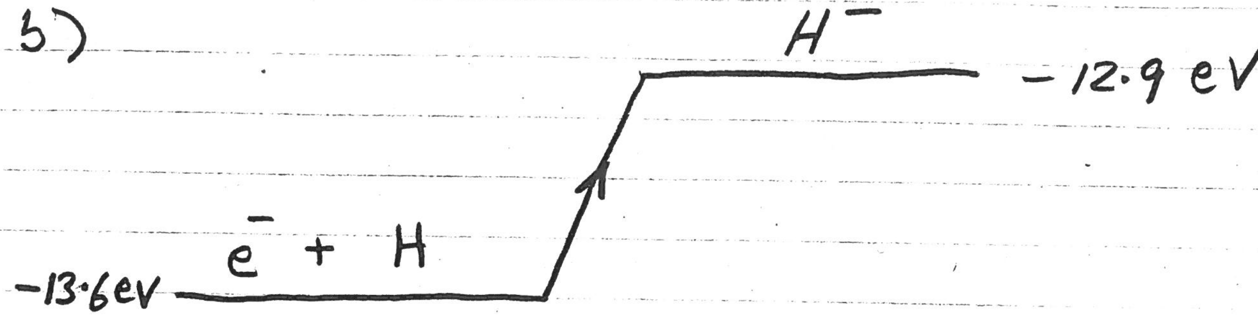
(Z' Seems "reasonable". $Z' = 0.6875$ is between the values $Z' = 0$ for perfect screening and $Z' = 1$ for no screening.)

optimal energy $E' = \left[(Z')^2 - \frac{11}{8}Z'\right]\frac{e^2}{4\pi\varepsilon_0 a_0}$ (Bohr radius $a_0 = 5.2918\times10^{-11}$ m)

$$E' = \left[\left(\frac{11}{16}\right)^2 - \frac{11}{8}\frac{11}{16}\right]\frac{(1.602\times10^{-19})^2}{4\pi(8.854\times10^{-12})(5.2918\times10^{-11})} = -2.060\times10^{-19}\text{ J} = -12.86\text{ eV}$$

(Q2 cont.)

b)



the reaction $e^- + H \rightarrow H^-$ has $\Delta E = +0.7$ eV predicted by the variational calculation in part a

increase in energy (67 kJ mol^{-1}) indicates H^- is an unstable anion (dissociates to lower energy $H + e^-$)

(Better energy calculations for H^- give -14.8 eV, suggesting that H^- is stable.)

Q3 a) $\psi(1,2) = f(1)\,g(2)\,\alpha(1)\,\alpha(2)$

$\psi(2,1) = f(2)\,g(1)\,\alpha(1)\,\alpha(2) \neq \psi(1,2)$
$\neq -\psi(1,2)$

neither symmetric nor antisymmetric

b) $\psi(1,2) = f(1)\,f(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

$\psi(2,1) = f(2)\,f(1)[\alpha(2)\beta(1) - \alpha(1)\beta(2)]$
$= -\psi(1,2)$ antisymmetric

(Q3 cont.)

c) $\psi(1,2,3) = f(1)\, f(2)\, f(3)\, \alpha(1)\, \alpha(2)\, \alpha(3)$

$= \psi(2,1,3)$

$= \psi(3,2,1)$

$= \psi(1,3,2)$

symmetric if $1,2;\ 1,3;\ 2,3$ interchanged

d) $\psi(1,2) = \exp[-a(r_1 - r_2)]$

$\psi(2,1) = \exp[-a(r_2 - r_1)] = 1/\psi(1,2)$

neither

e) $\psi(1,2) = [f(1)\, g(2) - f(2)\, g(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

$\psi(2,1) = [f(2)\, g(1) - f(1)\, g(2)][\alpha(2)\beta(1) - \alpha(1)\beta(2)]$

$= [f(1)\, g(2) - f(2)\, g(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

$= \psi(1,2)$ symmetric

f) $\psi(1,2) = \exp[-a(r_1 - r_2)^2]$

$\psi(2,1) = \exp[-a(r_2 - r_1)^2]$

$= \exp[-a(r_1 - r_2)^2]$

$= \psi(1,2)$

symmetric

Q4

$$\begin{aligned} 3c_1 + 4c_2 + c_3 &= 0 & \text{I} \\ c_1 + 3c_2 - 2c_3 &= 0 & \text{II} \\ c_1 - 2c_2 + 4c_3 &= 0 & \text{III} \end{aligned}$$

$$\begin{aligned} 3c_1 + 4c_2 + c_3 &= 0 & \text{I} \\ 3c_1 + 9c_2 - 6c_3 &= 0 & 3\text{II} = \text{IV} \\ 3c_1 - 6c_2 + 12c_3 &= 0 & 3\text{III} = \text{V} \end{aligned}$$

$$\begin{aligned} 3c_1 + 4c_2 + c_3 &= 0 & \text{I} \\ 0 - 5c_2 + 7c_3 &= 0 & \text{I} - \text{IV} = \text{VI} \\ 0 \quad 10c_2 - 11c_3 &= 0 & \text{I} - \text{V} = \text{VII} \end{aligned}$$

$$\begin{aligned} -10c_2 + 14c_3 &= 0 & 2\text{VI} \\ 10c_2 - 11c_3 &= 0 & \text{VII} \end{aligned}$$

$$3c_3 = 0 \qquad 2\text{VI} + \text{VII}$$

$c_3 = 0$

then $c_2 = 0$ (from VII) and $c_1 = 0$ (from I)

only the trivial solution $c_1 = c_2 = c_3 = 0$ exists

(Q4 cont.)

<u>or</u> Use the determinant test:

$$\begin{vmatrix} 3 & 4 & 1 \\ 1 & 3 & -2 \\ 1 & -2 & 4 \end{vmatrix} = 3\begin{vmatrix} 3 & -2 \\ -2 & 4 \end{vmatrix} - 4\begin{vmatrix} 1 & -2 \\ 1 & 4 \end{vmatrix} + 1\begin{vmatrix} 1 & 3 \\ 1 & -2 \end{vmatrix}$$

$$= 3(8) - 4(6) + 1(-5)$$

$$= 24 - 24 - 5$$

$$= -5$$

$$\neq 0$$

non-trivial solution does not exist