

Name _____ Student Number _____

Mid-Term #2

Show your work clearly. I will give partial credit in some cases, but *only* to the extent that I can clearly understand your work. The exam is marked out of 100 points.

You may use any non-internet-enabled calculator for the exam. You may not use any internet-enabled device (including e-readers, tablets, laptops, cellular phones, ...). You may not use any notes, books, or other materials.

6 questions @ 16 points each. [There are 4 “free points”]

1 Bonus questions worth 10 points (see the last page).

Key integrals and identities:

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \cos\left(\frac{n\pi x}{a}\right) \cos\left(\frac{m\pi x}{a}\right) dx$$

$$0 = \int_0^a \cos\left(\frac{n\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\frac{a^2}{4} = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 x dx$$

$$\left(\frac{a}{2\pi n}\right)^3 \left(\frac{4\pi^3 n^3}{3} - 2\pi n\right) = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 x^2 dx$$

$$\frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \int_0^\infty e^{-\alpha x^2} dx$$

$$\left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right) \left(\frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^n}\right) = \int_0^\infty x^{2n} e^{-\alpha x^2} dx \quad n = 1, 2, 3, \dots$$

$$\left(\frac{1}{2}\right) \left(\frac{n!}{\alpha^{n+1}}\right) = \int_0^\infty x^{2n+1} e^{-\alpha x^2} dx \quad n = 0, 1, 2, \dots$$

$$\int x \sin(bx) dx = \frac{\sin(bx)}{b^2} - \frac{x \cos(bx)}{b} + \text{constant}$$

$$\int x^2 \sin(bx) dx = -\left(\frac{x^2 \cos(bx)}{b} + \frac{2x \cos(bx + \frac{1}{2}\pi)}{b^2} + \frac{2 \cos(bx + \pi)}{b^3}\right) + \text{constant}$$

$$2 \sin(x) \sin(y) = \cos(x-y) - \cos(x+y) \quad \rightarrow \quad 2 \sin^2 x = 1 - \cos(2x)$$

$$2 \cos(x) \cos(y) = \cos(x-y) + \cos(x+y) \quad \rightarrow \quad 2 \cos^2 x = 1 + \cos(2x)$$

$$2 \sin(x) \cos(y) = \sin(\alpha + \beta) + \sin(\alpha - \beta) \quad \rightarrow \quad 2 \sin x \cos x = \sin(2x)$$

$$\sin(x+y) = \sin x \cos y + \cos x \sin y \quad \rightarrow \quad \sin(2x) = 2 \sin x \cos x$$

$$\cos(x+y) = \cos x \cos y - \sin x \sin y \quad \rightarrow \quad \cos(2x) = \cos^2 x - \sin^2 x$$

VALUES OF SOME PHYSICAL CONSTANTS

Constant	Symbol	Value
Avogadro's number	N_0	$6.02205 \times 10^{23} \text{ mol}^{-1}$
Proton charge	e	$1.60219 \times 10^{-19} \text{ C}$
Planck's constant	h	$6.62618 \times 10^{-34} \text{ J}\cdot\text{s}$
	\hbar	$1.05459 \times 10^{-34} \text{ J}\cdot\text{s}$
Speed of light in vacuum	c	$2.997925 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Atomic mass unit	amu	$1.66056 \times 10^{-27} \text{ kg}$
Electron rest mass	m_e	$9.10953 \times 10^{-31} \text{ kg}$
Proton rest mass	m_p	$1.67265 \times 10^{-27} \text{ kg}$
Boltzmann constant	k_B	$1.38066 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ 0.69509 cm^{-1}
Molar gas constant	R	$8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Permittivity of a vacuum	ϵ_0	$8.854188 \times 10^{-12} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
	$4\pi\epsilon_0$	$1.112650 \times 10^{-10} \text{ C}^2\cdot\text{s}^2\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$
Rydberg constant (infinite nuclear mass)	R_∞	$2.179914 \times 10^{-23} \text{ J}$ 1.097373 cm^{-1}
First Bohr radius	a_0	$5.29177 \times 10^{-11} \text{ m}$
Bohr magneton	μ_B	$9.27409 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
Stefan-Boltzmann constant	σ	$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

CONVERSION FACTORS FOR ENERGY UNITS

joule	$\text{kJ}\cdot\text{mol}^{-1}$	eV	au	cm^{-1}	Hz
1 joule = 1	6.022×10^{20}	6.242×10^{18}	2.2939×10^{17}	5.035×10^{22}	1.509×10^{13}
1 $\text{kJ}\cdot\text{mol}^{-1}$ = 1.661×10^{-21}	1	1.036×10^{-2}	3.089×10^{-4}	83.60	2.506×10^{12}
1 eV = 1.602×10^{-19}	96.48	1	3.675×10^{-2}	8065	2.418×10^{14}
1 au = 4.359×10^{-18}	2625	27.21	1	2.195×10^5	6.580×10^{15}
1 cm^{-1} = 1.986×10^{-23}	1.196×10^{-2}	1.240×10^{-4}	4.556×10^{-6}	1	2.998×10^{10}
1 Hz = 6.626×10^{-34}	3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}	1

SOME MATHEMATICAL FORMULAS

Paul

$$\sin \alpha \sin \beta = \frac{1}{2} \cos (\alpha - \beta) - \frac{1}{2} \cos (\alpha + \beta)$$

$$\cos \alpha \cos \beta = \frac{1}{2} \cos (\alpha - \beta) + \frac{1}{2} \cos (\alpha + \beta)$$

$$\sin \alpha \cos \beta = \frac{1}{2} \sin (\alpha + \beta) + \frac{1}{2} \sin (\alpha - \beta)$$

$$\sin (\alpha \pm \beta) = \sin \alpha \cos \beta \pm \cos \alpha \sin \beta$$

$$\cos (\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$$

$$e^{\pm i\theta} = \cos \theta \pm i \sin \theta$$

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2!} f''(a)(x-a)^2 + \frac{1}{3!} f'''(a)(x-a)^3 + \dots$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \dots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \dots$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \dots \quad x^2 < 1$$

$$(1 \pm xy)^n = 1 \pm nx \pm \frac{n(n-1)}{2!} x^2 \pm \frac{n(n-1)(n-2)}{3!} x^3 \pm \dots \quad x^2 < 1$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad (n \text{ positive integer})$$

$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a} \right)^{1/2}$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a} \right)^{1/2} \quad (n \text{ positive integer})$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \quad (n \text{ positive integer})$$

$$\int_0^a \sin \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx = \int_0^a \cos \frac{m\pi x}{a} \cos \frac{n\pi x}{a} dx = \frac{a}{2} \delta_{nm}$$

$$\int_0^a \cos \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx = 0 \quad (m \text{ and } n \text{ integers})$$

$$1 \text{ J (oule)} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 1 \text{ C (oulomb)}\cdot\text{V (olt)}$$

_____ 1. The vibrational transition of the deuterium dimer, D_2 , molecule from its ground vibrational state to its first excited vibrational state has $\bar{\nu}_{D_2} = 1/\lambda = 2994 \text{ cm}^{-1}$. The corresponding transition in the tritium dimer, T_2 , has about _____. The mass of a tritium atom is (to the accuracy we need) 3 u.

- (A) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{9}{4}$ (B) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{3}{2}$ (C) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \sqrt{\frac{3}{2}}$ (D) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2}$
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_____ 2. A rotational transition of the deuterium dimer, D_2 , molecule from its ground rotational state, $J = 0$, to its first excited rotational state, $J = 1$, has $\bar{\nu}_{D_2} = 1/\lambda = 30.4 \text{ cm}^{-1}$. The corresponding transition in the tritium dimer, T_2 , has about _____.

- (A) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{9}{4}$ (B) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{3}{2}$ (C) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \sqrt{\frac{3}{2}}$ (D) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2}$
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In an external electric field with strength F , the one-dimensional harmonic oscillator Hamiltonian changes to

$$\hat{H}(F) = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + Fx + \frac{1}{2}kx^2$$

For $F = 0$, the normalized ground-state and first excited state wavefunctions are

$$\begin{aligned}\psi_0(x) &= \left(\frac{k\mu}{\pi^2 \hbar^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k\mu}{4\hbar^2}} \right)} \\ \psi_1(x) &= \left(\frac{k\mu}{\pi^2 \hbar^2} \right)^{1/8} e^{-\left(x^2 \sqrt{\frac{k\mu}{4\hbar^2}} \right)} \left(2x \left(\frac{k\mu}{4\hbar^2} \right)^{1/4} \right)\end{aligned}$$

- 3. What is the the first-order change in the ground-state energy as a function of F when the field is weak, $[dE_0/dF]_{F=0}$?**

Problems 4-6.

For the cyanine dye $\text{R}_2\ddot{\text{N}}-\text{C}=\overset{+}{\text{N}}\text{R}_2$, neglecting the electron-electron repulsion, the simple one-dimensional particle-in-a-box model can be improved by adding harmonic confinement of electrons into the bonding regions. The resulting Hamiltonian, in atomic units, is

$$\begin{aligned}\hat{H} &\equiv -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{1}{2}\nabla_4^2 + V_{\text{p-in-box}}(x_1) + V_{\text{p-in-box}}(x_2) + V_{\text{p-in-box}}(x_3) + V_{\text{p-in-box}}(x_4) \\ &\quad + y_1^2 + z_1^2 + y_2^2 + z_2^2 + y_3^2 + z_3^2 + y_4^2 + z_4^2 \\ &= \sum_{i=1}^4 \left(-\frac{1}{2}\nabla_i^2 + V_{\text{p-in-box}}(x_i) + y_i^2 + z_i^2 \right)\end{aligned}$$

where you should recall that $\nabla_j^2 = \frac{d^2}{dx_j^2} + \frac{d^2}{dy_j^2} + \frac{d^2}{dz_j^2}$ and where the box-length is 6 atomic units,

$$V_{\text{p-in-box}}(x) = \begin{cases} 0 & 0 \leq x \leq 6 \text{ a.u.} \\ +\infty & \text{otherwise} \end{cases}$$

All the constants are given in atomic units ($\hbar = m_e = 1$).

4. Write an expression for the ground-state energy of this system in atomic units.

5. **Write expressions for the orbitals that are occupied in the ground state of this system. It is not essential to normalize the orbitals.** You can use the abbreviated notation for the harmonic-oscillator orbitals that is given above question #3.
6. **Write an expression for the total expected square-deviation of all four electrons from the center of the bond. (For each electron, this amounts to evaluating the expectation value $\langle y^2 + z^2 \rangle$.)**

BONUS: Suppose that you are given two linear Hermitian operators, \hat{A} and \hat{B} , and you are told that $[\hat{A}, \hat{B}] = 0$. Assume furthermore that the eigenvalues of the operators are distinct,

$$\hat{A}\psi_m(x) = \alpha_m\psi_m(x) \quad \alpha_0 < \alpha_1 < \alpha_2 < \dots$$

$$\hat{B}\phi_n(x) = \beta_n\phi_n(x) \quad \beta_0 < \beta_1 < \beta_2 < \dots$$

Show that every eigenvector of \hat{A} is also an eigenvector of \hat{B} .

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Bohr magneton	μ_B	$9.27409 \times 10^{-24} \text{ J}\cdot\text{T}^{-1}$
Stefan-Boltzmann constant	σ	$5.67032 \times 10^{-8} \text{ J}\cdot\text{m}^{-2}\cdot\text{K}^{-4}\cdot\text{s}^{-1}$

CONVERSION FACTORS FOR ENERGY UNITS

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1 $\text{kJ}\cdot\text{mol}^{-1}$ = 1.661×10^{-21}	1	1.036×10^{-2}	3.089×10^{-4}	83.60	2.506×10^{12}
1 eV = 1.602×10^{-19}		1	3.675×10^{-2}	8065	2.418×10^{14}
1 au = 4.359×10^{-18}			1	2.195×10^5	6.580×10^{15}
1 cm^{-1} = 1.986×10^{-23}				1	2.998×10^{10}
1 Hz = 6.626×10^{-34}	3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}	1

SOME MATHEMATICAL FORMULAS

Paul

$$\sin \alpha \sin \beta = \frac{1}{2} \cos (\alpha - \beta) - \frac{1}{2} \cos (\alpha + \beta)$$

$$\cos \alpha \cos \beta = \frac{1}{2} \cos (\alpha - \beta) + \frac{1}{2} \cos (\alpha + \beta)$$

$$\sin \alpha \cos \beta = \frac{1}{2} \sin (\alpha + \beta) + \frac{1}{2} \sin (\alpha - \beta)$$

$$\sin (\alpha \pm \beta) = \sin \alpha \cos \beta \pm \cos \alpha \sin \beta$$

$$\cos (\alpha \pm \beta) = \cos \alpha \cos \beta \mp \sin \alpha \sin \beta$$

$$e^{\pm i\theta} = \cos \theta \pm i \sin \theta$$

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2!} f''(a)(x-a)^2 + \frac{1}{3!} f'''(a)(x-a)^3 + \dots$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \dots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \dots$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \dots \quad x^2 < 1$$

$$(1 \pm xy)^n = 1 \pm nx \pm \frac{n(n-1)}{2!} x^2 \pm \frac{n(n-1)(n-2)}{3!} x^3 \pm \dots \quad x^2 < \frac{1}{n}$$

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad (n \text{ positive integer})$$

$$\int_0^\infty e^{-ax^2} dx = \left(\frac{\pi}{4a} \right)^{1/2}$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdot \dots \cdot (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a} \right)^{1/2} \quad (n \text{ positive integer})$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}} \quad (n \text{ positive integer})$$

$$\int_0^a \sin \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx = \int_0^a \cos \frac{m\pi x}{a} \cos \frac{n\pi x}{a} dx = \frac{a}{2} \delta_{nm}$$

$$\int_0^a \cos \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx = 0 \quad (m \text{ and } n \text{ integers})$$

$$2 \quad \text{Joule} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 1 \text{ Coulomb}\cdot\text{Volt}$$

__E__ 1. The vibrational transition of the deuterium dimer, D_2 , molecule from its ground vibrational state to its first excited vibrational state has $\bar{\nu}_{D_2} = 1/\lambda = 2994 \text{ cm}^{-1}$. The corresponding transition in the tritium dimer, T_2 , has about

- (A) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{9}{4}$ (B) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{3}{2}$ (C) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \sqrt{\frac{3}{2}}$ (D) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2}$
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The reduced mass of D_2 is $\mu_{D_2} = \frac{2 \cdot 2}{2+2} = 1 \text{ u}$ and the reduced mass of T_2 is $\mu_{T_2} = \frac{3 \cdot 3}{3+3} = \frac{3}{2} \text{ u}$. The energy of the transition is

$$\Delta E = \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} (3) - \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} (1) = \hbar \sqrt{\frac{k}{\mu}}$$

$$= \frac{hc}{\lambda} = hc\bar{\nu}$$

So $\bar{\nu}$ is proportional to $\frac{1}{\sqrt{\mu}}$. So if μ increases by $\frac{3}{2}$ then $\bar{\nu}$ decreases by $\frac{1}{\sqrt{\frac{3}{2}}} = \sqrt{\frac{2}{3}}$. This is E

__F__ 2. A rotational transition of the deuterium dimer, D_2 , molecule from its ground rotational state, $J = 0$, to its first excited rotational state, $J = 1$, has $\bar{\nu}_{D_2} = 1/\lambda = 30.4 \text{ cm}^{-1}$. The corresponding transition in the tritium dimer, T_2 , has about

- (A) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{9}{4}$ (B) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{3}{2}$ (C) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \sqrt{\frac{3}{2}}$ (D) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2}$
 (E) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \sqrt{\frac{2}{3}}$ **(F) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{2}{3}$** (G) $\bar{\nu}_{T_2} = \bar{\nu}_{D_2} \cdot \frac{4}{9}$ (H) none of the above.

In the rigid rotor approximation, the rotational energy levels look like $E(J) = \frac{\hbar^2}{2\mu r_e^2} J(J+1)$. So the rotational transition in question has $\Delta E = \frac{\hbar^2}{2\mu r_e^2} (2) - \frac{\hbar^2}{2\mu r_e^2} (0)$. So, using again $\Delta E = hc\bar{\nu}$ we see that $\bar{\nu}$ is proportional to $\frac{1}{\mu}$. So if μ increases by $\frac{3}{2}$ then $\bar{\nu}$ decreases by $\frac{1}{\frac{3}{2}} = \frac{2}{3}$. This is choice F.

In an external electric field with strength F , the one-dimensional harmonic oscillator Hamiltonian changes to

$$\hat{H}(F) = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + Fx + \frac{1}{2}kx^2$$

For $F = 0$, the normalized ground-state and first excited state wavefunctions are

$$\begin{aligned}\psi_0(x) &= \left(\frac{k\mu}{\pi^2\hbar^2}\right)^{1/8} e^{-\left(x^2\sqrt{\frac{k\mu}{4\hbar^2}}\right)} \\ \psi_1(x) &= \left(\frac{k\mu}{\pi^2\hbar^2}\right)^{1/8} e^{-\left(x^2\sqrt{\frac{k\mu}{4\hbar^2}}\right)} \left(2x\left(\frac{k\mu}{4\hbar^2}\right)^{1/4}\right)\end{aligned}$$

3. What is the the first-order change in the ground-state energy as a function of F when the field is weak, $[dE_0/dF]_{F=0}$?

One way to understand this is that if you change the field from $-F$ to $+F$, this cannot change the system in any real way, since the direction of the field is irrelevant. This means that $F = 0$ must either be a maximum or a minimum in the field; therefore it must be that $[dE_0/dF]_{F=0} = 0$.

However, this can be worked out directly, and quite simply, using the Hellmann-Feynman theorem.

$$\begin{aligned}\left.\frac{\partial E}{\partial F}\right|_{F=0} &= \int_{-\infty}^{\infty} \psi_{0;F=0}^*(x) \left[\frac{\partial \hat{H}}{\partial F}\right]_{F=0} \psi_{0;F=0}(x) dx \\ &= \int_{-\infty}^{\infty} x \left(\left(\frac{k\mu}{\pi^2\hbar^2}\right)^{1/8} e^{-\left(x^2\sqrt{\frac{k\mu}{4\hbar^2}}\right)}\right)^2 dx \\ &= \left(\frac{k\mu}{\pi^2\hbar^2}\right)^{1/4} \int_{-\infty}^{\infty} x e^{-2\left(x^2\sqrt{\frac{k\mu}{4\hbar^2}}\right)} dx \\ &= 0\end{aligned}$$

This integral is zero because it is the integral of an odd function. That is, if you look at the function, it's clear that the integral from $-\infty < x \leq 0$ is equal to minus one times the integral from $0 \leq x < \infty$, and so the integral from minus infinity to plus infinity is zero. Yet another way of thinking about this is that the integral in the next-to-last-equation is proportional to the integral $\int_{-\infty}^{\infty} \psi_1^*(x) \psi_0(x) dx = 0$, which is zero because the eigenfunctions are orthogonal.

Problems 4-6.

For the cyanine dye $\text{R}_2\ddot{\text{N}}-\text{C}=\text{N}^+\text{R}_2$, neglecting the electron-electron repulsion, the simple one-dimensional particle-in-a-box model can be improved by adding harmonic confinement of electrons into the bonding regions. The resulting Hamiltonian, in atomic units, is

$$\hat{H} \equiv -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{1}{2}\nabla_4^2 + V_{\text{p-in-box}}(x_1) + V_{\text{p-in-box}}(x_2) + V_{\text{p-in-box}}(x_3) + V_{\text{p-in-box}}(x_4) \\ + y_1^2 + z_1^2 + y_2^2 + z_2^2 + y_3^2 + z_3^2 + y_4^2 + z_4^2$$

where you should recall that $\nabla_j^2 = \frac{d^2}{dx_j^2} + \frac{d^2}{dy_j^2} + \frac{d^2}{dz_j^2}$ and where the box-length is 6 atomic units,

$$V_{\text{p-in-box}}(x) = \begin{cases} 0 & 0 \leq x \leq 6 \text{ a.u.} \\ +\infty & \text{otherwise} \end{cases}$$

All the constants are given in atomic units ($\hbar = m_e = 1$).

4. Write an expression for the ground-state energy of this system in atomic units.

I can write this Hamiltonian as a sum of Hamiltonians that I know, namely,

$$\hat{H} = \sum_{i=1}^4 \left(-\frac{1}{2} \frac{d^2}{dx_i^2} + V_{\text{p-in-box}}(x_i) \right) + \sum_{i=1}^4 \left(-\frac{1}{2} \frac{d^2}{dy_i^2} + \frac{1}{2} k y_i^2 \right) + \sum_{i=1}^4 \left(-\frac{1}{2} \frac{d^2}{dz_i^2} + \frac{1}{2} k z_i^2 \right) \\ = \sum_{i=1}^4 \left(-\frac{1}{2} \nabla_i^2 + V_{\text{p-in-box}}(x_i) + \frac{1}{2} k (y_i^2 + z_i^2) \right)$$

where I've chosen to write $k = 2 \text{ a.u.}$, just to make my life a little simpler. Now I have

$$E_{n_{x1}, n_{x2}, n_{x3}, n_{x4}, n_{y1}, n_{y2}, n_{y3}, n_{y4}, n_{z1}, n_{z2}, n_{z3}, n_{z4}} = \frac{\hbar^2 (n_{x1}^2 + n_{x2}^2 + n_{x3}^2 + n_{x4}^2)}{8m_e a^2} \\ + \frac{\hbar \omega}{2} (2n_{y1} + 1 + 2n_{y2} + 1 + 2n_{y3} + 1 + 2n_{y4} + 1) \\ + \frac{\hbar \omega}{2} (2n_{z1} + 1 + 2n_{z2} + 1 + 2n_{z3} + 1 + 2n_{z4} + 1) \\ = \frac{(2\pi)^2 \hbar^2 (n_{x1}^2 + n_{x2}^2 + n_{x3}^2 + n_{x4}^2)}{8m_e a^2} + \frac{\hbar}{2} \left(\sqrt{\frac{k}{m_e}} \right) \left(8 + 2 \left(n_{y1} + n_{y2} + n_{y3} + n_{y4} \right. \right. \\ \left. \left. + n_{z1} + n_{z2} + n_{z3} + n_{z4} \right) \right) \\ = \sum_{i=1}^4 \left[\frac{(2\pi)^2 \hbar^2 n_{xi}^2}{8m_e a^2} + \frac{\hbar}{2} \sqrt{\frac{k}{m_e}} (2n_{yi} + 2n_{zi} + 2) \right] \\ = \sum_{i=1}^4 \left[\frac{(2\pi)^2 n_{xi}^2}{8 \cdot 6^2} + \sqrt{2} (n_{yi} + n_{zi} + 1) \right]$$

Now I know that $\hbar = m_e = 1; k = 2; a = 6$. So*

$$E_{n_{x1}, n_{x2}, n_{x3}, n_{x4}, n_{y1}, n_{y2}, n_{y3}, n_{y4}, n_{z1}, n_{z2}, n_{z3}, n_{z4}} = \frac{(2\pi)^2 (n_{x1}^2 + n_{x2}^2 + n_{x3}^2 + n_{x4}^2)}{8(6)^2} + \frac{1}{2}(\sqrt{2}) \left(8 + 2 \left(n_{y1} + n_{y2} + n_{y3} + n_{y4} + n_{z1} + n_{z2} + n_{z3} + n_{z4} \right) \right)$$

$$= \frac{(2\pi)^2 (n_{x1}^2 + n_{x2}^2 + n_{x3}^2 + n_{x4}^2)}{288} + \sqrt{2} \left(4 + \left(n_{y1} + n_{y2} + n_{y3} + n_{y4} + n_{z1} + n_{z2} + n_{z3} + n_{z4} \right) \right)$$

Now I need to figure out the ground state. I can put two electrons in the state with $n_x = 1; n_y = n_z = 0$. This state has energy

$$\varepsilon(n_x = 1; n_y = 0; n_z = 0) = \frac{(2\pi)^2 1}{288} + \sqrt{2} = 1.551 \text{ a.u.}$$

The next two electrons need to go in a state with either the harmonic oscillator part or the particle-in-a-box part excited. The energy of the two possible states are:

$$\varepsilon(n_x = 2, n_y = n_z = 0) = \frac{(2\pi)^2 (4)}{288} + \sqrt{2} = 1.963 \text{ a.u.}$$

$$\varepsilon(n_x = 1, n_y = 1; n_z = 0) = \frac{(2\pi)^2 (1)}{288} + \sqrt{2} (1+1) = 2.966 \text{ a.u.}$$

So the first state is occupied. This means that the energy for four electrons in this system is:

$$E_{g.s.} = 2 \cdot E(n_x = 1; n_y = n_z = 0) + 2 \cdot E(n_x = 2, n_y = n_z = 0) = 2 \cdot 1.551 + 2 \cdot 1.963 = 7.028 \text{ a.u.}$$

$$= E_{112200000000}$$

where in the second line I've used the notation from the *d equation above.

5. Write expressions for the orbitals that are occupied in the ground state of this system. It is not essential to normalize the orbitals. You can use the abbreviated notation for the harmonic-oscillator orbitals that is given above question #3.

The orbitals are products of the wavefunctions. So, using the particle-in-a-box wavefunctions

$$\phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) = \sqrt{\frac{2}{6}} \sin\left(\frac{n\pi x}{6}\right) = \sqrt{\frac{1}{3}} \sin\left(\frac{1}{6} n\pi x\right)$$

and the harmonic-oscillator wavefunction from problem #3,

$$\psi_0(y) = \left(\frac{k\mu}{\pi^2 \hbar^2}\right)^{1/8} e^{-\left(y^2 \sqrt{\frac{k\mu}{4\hbar^2}}\right)} = \left(\frac{2}{\pi^2}\right)^{1/8} e^{-\left(y^2 \sqrt{\frac{2}{4}}\right)} = \left(\frac{2}{\pi^2}\right)^{1/8} e^{-\left(\frac{y^2}{\sqrt{2}}\right)}$$

The occupied orbitals are:

$$\begin{aligned} \phi_1(x) \psi_0(y) \psi_0(z) \alpha(1) \\ \phi_1(x) \psi_0(y) \psi_0(z) \beta(1) \\ \phi_2(x) \psi_0(y) \psi_0(z) \alpha(1) \\ \phi_2(x) \psi_0(y) \psi_0(z) \beta(1) \end{aligned}$$

6. Write an expression for the total expected square-deviation of all four electrons from the center of the bond. (For each electron, this amount to evaluating the expectation value $\langle y^2 + z^2 \rangle$.)

This means that we need to evaluate the expectation value

$$\left\langle \sum_{i=1}^4 (y_i^2 + z_i^2) \right\rangle = \int \Psi^* (x_1, y_1, z_1, \dots, x_4, y_4, z_4) \left(\sum_{i=1}^4 (y_i^2 + z_i^2) \right) \Psi (x_1, y_1, z_1, \dots, x_4, y_4, z_4) dx_1 dy_1 dz_1 \dots dx_4 dy_4 dz_4$$

However, let's look at the Hamiltonian,

$$\begin{aligned} \hat{H} &= \sum_{i=1}^4 \left(-\frac{1}{2} \frac{d^2}{dx_i^2} + V_{\text{p-in-box}}(x_i) \right) + \sum_{i=1}^4 \left(-\frac{1}{2} \frac{d^2}{dy_i^2} + \frac{1}{2} k y_i^2 \right) + \sum_{i=1}^4 \left(-\frac{1}{2} \frac{d^2}{dz_i^2} + \frac{1}{2} k z_i^2 \right) \\ \frac{\partial \hat{H}}{\partial k} &= \sum_{i=1}^4 \left(\frac{1}{2} y_i^2 + \frac{1}{2} z_i^2 \right) = \frac{1}{2} \sum_{i=1}^4 (y_i^2 + z_i^2) \\ 2 \frac{\partial \hat{H}}{\partial k} &= \sum_{i=1}^4 (y_i^2 + z_i^2) \end{aligned}$$

Therefore,

$$\begin{aligned} \left\langle \sum_{i=1}^4 (y_i^2 + z_i^2) \right\rangle &= \int \Psi^* (x_1, y_1, z_1, \dots, x_4, y_4, z_4) \left[2 \left(\frac{\partial \hat{H}}{\partial k} \right) \right] \Psi (x_1, y_1, z_1, \dots, x_4, y_4, z_4) dx_1 dy_1 dz_1 \dots dx_4 dy_4 dz_4 \\ &= 2 \frac{\partial E}{\partial k} \end{aligned}$$

In the last line I used the Hellmann-Feynman theorem. Then, using the energy expression I have (from problem #4) I have

$$\begin{aligned} E &= \frac{(2\pi)^2 \hbar^2 (n_{x1}^2 + n_{x2}^2 + n_{x3}^2 + n_{x4}^2)}{8m_e a^2} + \frac{\hbar}{2} \left(\sqrt{\frac{k}{m_e}} \right) \left(8 + 2 \left(\begin{matrix} n_{y1} + n_{y2} + n_{y3} + n_{y4} \\ + n_{z1} + n_{z2} + n_{z3} + n_{z4} \end{matrix} \right) \right) \\ &= \sum_{i=1}^4 \left[\frac{(2\pi)^2 \hbar^2 n_{xi}^2}{8m_e a^2} + \frac{\hbar}{2} \sqrt{\frac{k}{m_e}} (2n_{yi} + 2n_{zi} + 2) \right] \\ \left. \frac{\partial E}{\partial k} \right|_{k=2} &= \sum_{i=1}^4 \left[\frac{1}{2} \frac{\hbar}{2} \frac{1}{\sqrt{k m_e}} (2n_{yi} + 2n_{zi} + 2) \right] \\ &= \frac{1}{2} \sum_{i=1}^4 \left[\frac{1}{\sqrt{2}} (n_{yi} + n_{zi} + 1) \right] \\ &= \frac{1}{2} \sum_{i=1}^4 \left[\frac{1}{\sqrt{2}} (0 + 0 + 1) \right] \\ &= \frac{4}{2\sqrt{2}} = \frac{2}{\sqrt{2}} \end{aligned}$$

and so:

$$\left\langle \sum_{i=1}^4 (y_i^2 + z_i^2) \right\rangle = 2 \cdot \frac{2}{\sqrt{2}} = \frac{4}{\sqrt{2}} = 2.828 \text{ (a.u.)}^2$$

BONUS: Suppose that you are given two linear Hermitian operators, \hat{A} and \hat{B} , and you are told that $[\hat{A}, \hat{B}] = 0$. Assume furthermore that the eigenvalues of the operators are distinct,

$$\hat{A}\psi_m(x) = \alpha_m \psi_m(x) \quad \alpha_0 < \alpha_1 < \alpha_2 < \dots$$

$$\hat{B}\phi_n(x) = \beta_n \phi_n(x) \quad \beta_0 < \beta_1 < \beta_2 < \dots$$

Show that every eigenvector of \hat{A} is also an eigenvector of \hat{B} .

I know that $[\hat{A}, \hat{B}]\psi(x) = 0$ for every wavefunction. Let's assume, then, that $\psi(x)$ is an eigenvector of \hat{A} . Then

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi_m(x) = 0$$

$$\hat{A}\hat{B}\psi_m(x) = \hat{B}\hat{A}\psi_m(x)$$

$$\hat{A}[\hat{B}\psi_m(x)] = \hat{B}\alpha_m\psi_m(x) = \alpha_m[\hat{B}\psi_m(x)]$$

In the third line I used the fact that $\psi_m(x)$ was an eigenfunction of \hat{A} and I used the fact that \hat{B} was a linear operator. Note, however, that this equation means that $\hat{B}\psi_m(x)$ must be an eigenfunction of \hat{A} with eigenvalue α_m . This means that $\hat{B}\psi_m(x)$ is proportional to $\psi_m(x)$, or that there is some number, β_m , such that $\hat{B}\psi_m(x) = \beta_m\psi_m(x)$. That is, if \hat{A} and \hat{B} commute, and if the eigenvalues of \hat{A} are distinct, then every eigenvector of \hat{A} is also an eigenvector of \hat{B} .