

Exam 2 Solution Set

Useful numbers and plots you may need are at the end.
You must upload your answer (PDF or JPEG) by 10:55 on Moodle to get full credit.

1. (11 pts) The equilibrium internuclear distance of nitric oxide, NO is 0.1152 nm. Let's find its unique rotational fingerprint to four significant figures. The masses of ^{14}N and ^{16}O are 14.007 and 15.995 grams per mole, respectively.

a. (2 pts) **Calculate** the reduced mass ' μ ' of the NO molecule in kg. (Not kg/mole, just one molecule.)

$$\mu = \frac{14.007 * 15.995}{14.007 + 15.995} * 1.661 \times 10^{-27} \text{ kg} = 1.240 * 10^{-26} \frac{\text{kg}}{\text{molecule}}$$

b. (2 pts) **Calculate** the moment of inertia μr^2 of the NO molecule in kg m^2 .

$$I = \mu r^2 = 1.240 * 10^{-26} * (0.1152 * 10^{-9})^2 = 1.645 * 10^{-46} \text{ kg m}^2$$

c. (2 pts) **Write down** the formula for the rotational energy in terms of \hbar , μ , r and angular momentum J . [Remember, NO rotates in three dimensions.]

$$E = \frac{\hbar^2}{2\mu R^2} J(J + 1)$$

d. (2 pts) **Calculate** the energy difference between the $J=0$ and $J=1$ energy level in Joules.

$$\Delta E = \frac{\hbar^2}{2I} (2 - 0)$$
$$\Delta E = \frac{(1.055 * 10^{-34})^2}{(1.645 * 10^{-46})} = 6.766 * 10^{-23} \text{ J}$$

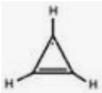
e. (2 pts) **Calculate** the wavelength of light that would excite this transition

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 * 10^{-34} * 2.998 * 10^8}{6.766 * 10^{-23}} = 2.935 \text{ mm}$$

You would be using a radiotelescope or "mm wave antenna" to look for this molecule.

f. (1 pt) Any conclusions about an exoplanet if you found significant concentrations of NO, ozone and fluorocarbons in its atmosphere by detecting their rotational transitions with a radiotelescope?

Potential signs of a civilization that produces oxidants and naturally extremely rare carbon compounds (containing fluorine).

2. (18 pts) Find the Hückel molecular orbitals and energies of the cyclopropenyl radical . This is like the allyl radical, but the first and third π electron now ALSO have an overlap matrix element β because the molecule is a ring. Remember, $\beta < 0$.

a. (2+ 2 pts) **Write down** the matrix to be diagonalized, and then **write down** the determinant you need to solve in terms of α , β and the eigenvalues E.

$$\begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix} \text{ and } \begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

b. (2 pts) **Simplify your notation** by dividing every element of the determinant by β , and then using $x = (\alpha - E)/\beta$.

$$\begin{pmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{pmatrix} = 0$$

c. (3 pts) **Multiply out** the 3x3 determinant to get the polynomial for x.

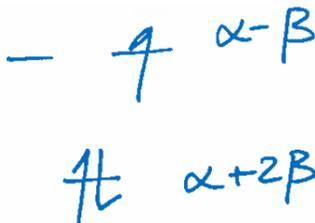
$$x^3 - 3x + 2 = 0$$

d. (2 pts) **Find** the three eigenvalues E as a function of α and β . [Hint: the cubic equation $y^3 - 3y + 2 = 0$ has solutions -2, 1 and 1]

$$E_1 = \alpha + 2\beta$$

$$E_2 = E_3 = \alpha - \beta$$

d. (3 pts) **Draw** the energy level diagram and fill in the three π electrons to give the lowest energy state.



e. (4 pts) **Find** the orthonormal eigenvector for the lowest energy orbital; if you used an online matrix tool, **show** a screenshot of your calculation. **Sketch** the molecular orbital using the usual “8” shape to symbolize each p orbital and **shading** one lobe to indicate the (-) sign.

For the lowest energy orbital $x = -2$. (Note that it makes no difference whether you do it with the determinant in units of energy (α , β) or unitless (x , 1) as long as you normalize at the end.)

$$\begin{pmatrix} -2 & 1 & 1 \\ 1 & -2 & 1 \\ 1 & 1 & -2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \Rightarrow$$

$-2c_1 + c_2 + c_3 = 0$ and $c_1 - 2c_2 + c_3 = 0$ (the third equation is not linearly independent and normalization will obtain the final value of the c_i). Subtracting the two equations,

$-3c_1 + 3c_2 = 0$ or $c_1 = c_2$. Then from the first equation, $c_3 = c_1$. So all three coefficients are equal: the lowest energy orbital is a fully bonding orbital. Normalizing, $(1/\sqrt{3})^2 + (1/\sqrt{3})^2 + (1/\sqrt{3})^2 = 1$, so

$$c_1 = c_2 = c_3 = \frac{1}{\sqrt{3}}, \text{ or } \psi_1 = \frac{1}{\sqrt{3}}\phi_1 + \frac{1}{\sqrt{3}}\phi_2 + \frac{1}{\sqrt{3}}\phi_3$$



(11 pts) Consider an electron confined on a surface in a square box of side $L = 1.00$ nm, at an energy level given by $5h^2/(8m_eL^2)$.

a. (2+2 pts) **What are** the possible values for the quantum numbers n_x and n_y , and **what is** the degeneracy of this state?

$$n_x = 1, n_y = 2$$

$$n_y = 2, n_x = 1$$

degeneracy is 2.

b. (2+3+2 pts) If you fill three electrons into this box according to the Pauli exclusion principle, **what is** the longest wavelength light that can be absorbed? Start by **writing down** the formula for the corresponding energy difference with the correct quantum numbers, then **write the formula** relating wavelength to energy.

The lowest energy transition is by absorbing light that excites an electron from

The formulas thus are $n_x=1, n_y=1$ to $n_x=2, n_y=1$

$$\Delta E = (5 - 2) \frac{h^2}{8mL^2} \text{ (3 pts) and } \lambda = \frac{hc}{\Delta E} \text{ (2 pts)}$$

$$\Delta E = (5 - 2) \frac{(6.626 * 10^{-34})^2}{8(9.109 * 10^{-31})(1.00 * 10^{-9})^2} = 1.81 * 10^{-19} \text{ J}$$

$$1.099 * 10^{-6} \text{ m (about 1100 nm) (2 pts)}$$

This lies in the near infrared, a wavelength region important for night vision equipment.

4. (12 pts) Here you will use the identity operator to prove a useful relationship.

a. (2 pts) **Write down** the identity operator in Dirac bracket notation in terms of a summation and the basis kets $|n\rangle$.

$$I = \sum_n |n\rangle\langle n|$$

b. (2 pts) **Write down** the same identity operator in function and integral notation, i.e. using basis functions $\phi_n(x)$ and a placeholder $___$ where a function should be inserted.

$$I = \sum_n \phi_n(x) \int \phi_n^*(x) ___$$

c. (4 pts) Using “a.”, **show** that if operator \hat{H} has real eigenvalues, then the matrix element $H_{AB} = H_{BA}^*$ (in other words, show that $\langle A|\hat{H}|B\rangle = \langle B|\hat{H}|A\rangle^*$). This “Hermitian property” saves us calculating half the matrix elements to get the eigenvalues of the energy!

$$\begin{aligned}
 \langle B|\hat{H}|A\rangle^* &= \left(\sum_n \langle B|\hat{H}|n\rangle \langle n|A\rangle \right)^* \\
 &= \left(\sum_m \sum_n \langle B|m\rangle \langle m|\hat{H}|n\rangle \langle n|A\rangle \right)^* \\
 &= \left(\sum_n \langle B|n\rangle \langle n|\hat{H}|n\rangle \langle n|A\rangle \right)^* \\
 &= \sum_n \langle B|n\rangle^* \langle n|\hat{H}|n\rangle^* \langle n|A\rangle^* \\
 &= \sum_n \langle n|B\rangle \langle n|\hat{H}|n\rangle \langle A|n\rangle \\
 &= \sum_n \langle A|n\rangle \langle n|\hat{H}|n\rangle \langle n|B\rangle \\
 &= \sum_m \sum_n \langle A|m\rangle \langle m|\hat{H}|n\rangle \langle n|B\rangle \\
 &= \langle A|\hat{H}|B\rangle
 \end{aligned}$$

First step: insert an identity; second step: insert another identity; third step: $|n\rangle$ are eigenfunctions of \hat{H} , so all the off-diagonal elements are zero; fourth step: write out the complex conjugates; fifth step: $\langle x|y\rangle = \langle y|x\rangle^*$ as proved in class; sixth step: flip the order of the first and third term; seventh step: you can add a sum over m since $\langle m|\hat{H}|n\rangle = 0$ anyway unless $m=n$; final step: the two identities can be removed.

d. (4 pts) **Write down** the exact same proof as in “c”, but using integral notation and basis functions $\varphi_n(x)$ instead of bracket notation. [Tip: call “ $|A\rangle$ ” “ ψ_A ” and “ $|B\rangle$ ” “ ψ_B ”, and substitute your answer to **b.** for every identity, making sure that each different integral gets a different integration variable like x, x', x'' etc.]

$$\begin{aligned}
 \left(\int dx \psi_B^*(x) \hat{H} \psi_A(x) \right)^* &= \left(\sum_n \int dx \psi_B^*(x) \hat{H} \varphi_n(x) \int dx' \varphi_n^*(x') \psi_A(x') \right)^* \\
 &= \sum_m \sum_n \int dx \psi_B^*(x) \varphi_m(x) \int dx'' \varphi_m^*(x'') \hat{H} \varphi_n(x'') \int dx' \varphi_n^*(x') \psi_A(x') \Big)^* \\
 &= \left(\sum_n \int dx \psi_B^*(x) \varphi_n(x) \int dx'' \varphi_n^*(x'') \hat{H} \varphi_n(x'') \int dx' \varphi_n^*(x') \psi_A(x') \right)^* \\
 &= \sum_n \int dx \psi_B(x) \varphi_n^*(x) \int dx'' \varphi_n(x'') \hat{H} \varphi_n^*(x'') \int dx' \varphi_n(x') \psi_A^*(x') \\
 \\
 &= \sum_n \int dx \varphi_n^*(x) \psi_B(x) \int dx'' \varphi_n(x'') \hat{H} \varphi_n^*(x'') \int dx' \psi_A^*(x') \varphi_n(x') \\
 &= \sum_n \int dx' \psi_A^*(x') \varphi_n(x') \int dx'' \varphi_n^*(x'') \hat{H} \varphi_n(x'') \int dx \varphi_n^*(x) \psi_B(x) \\
 &= \sum_m \sum_n \int dx' \psi_A^*(x') \varphi_m(x') \int dx'' \varphi_m^*(x'') \hat{H} \varphi_n(x'') \int dx \varphi_n^*(x) \psi_B(x) \\
 &\qquad \int dx \psi_A^*(x) \hat{H} \psi_B(x)
 \end{aligned}$$

We think the bracket version is a little less of a hassle to write out!

Useful numbers:

1 atomic mass unit = 1.661×10^{-27} kg; mass of electron $m_e = 9.109 \times 10^{-31}$ kg

Planck's constant $h = 6.626 \times 10^{-34}$ J·s; note that $\hbar = h/2\pi$ is about 6.28 times smaller.

1 mole $\approx 6.0221 \times 10^{23}$ particles; 1 kg = 1000 g

1 Å = 0.1 nm = 100 pm; $c = 2.99792458 \cdot 10^8$ m/s

