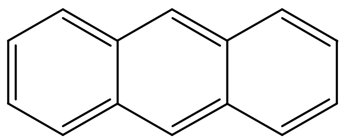
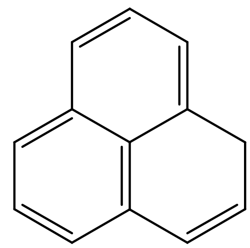
Quiz 4
CHEM 325
Spring 2009

Name: ____

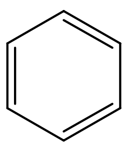
1. (5 Points) Assign the following molecules to the proper point group. Ignore the positions of double bonds in the aromatic rings.



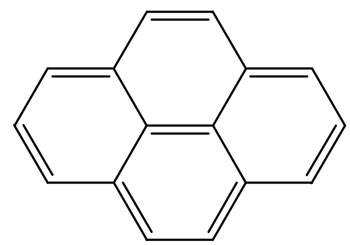
D_{2h}



D_{3h}



D_{6h}



D_{2h}

2. (4 Points) In time-independent non-degenerate perturbation theory in order for an excited state (ψ_1) to contribute to the first-order correction to the ground state (ψ_0) energy, the integral $\langle \psi_1 | \hat{H} | \psi_0 \rangle$ must not equal zero. In C_{2v} symmetry the ground state wavefunction transforms as A_1 and an excited state transforms as A_2. Can the integral $\langle \psi_1 | \hat{H} | \psi_0 \rangle$ be non-zero for these states? Explain.

The Hamiltonian always transforms as A_1, so we simply need to determine whether the triple direct product A_2 x A_1 x A_1 contains the totally symmetric representation, A_1. Since A_1 x A_1 = A_1 and A_2 x A_1 = A_2, we may write A_2 x A_1 x A_1 = A_2. Because the triple direct product does not contain A_1, the integral is zero.

3. Let the wavefunction ψ be a linear combination of the orthonormal wavefunctions ϕ_1 and ϕ_2 defined as $\psi = a\phi_1 + b\phi_2$, where a and b are arbitrary constants.

a. (5 Points) Normalize ψ.

The normalization condition is $\int N^2\psi^*\psi d\tau = 1$**. Substituting in the given** ψ **yields** $N^2\int\left(a\phi_1^* + b\phi_2^*\right)\left(a\phi_1 + b\phi_2\right)d\tau = 1$**, which may be expanded to give** $N^2\int a^2\phi_1^*\phi_1 + ab\phi_1^*\phi_2 + ab\phi_2^*\phi_1 + b^2\phi_2^*\phi_2 d\tau = 1$**.**

The integral of a sum is equal to the sum of the individual integrals, so we may write

$$N^2\left(a^2\int\phi_1^*\phi_1 d\tau + ab\int\phi_1^*\phi_2 d\tau + ab\int\phi_2^*\phi_1 d\tau + b^2\int\phi_2^*\phi_2 d\tau\right) = 1$$

Any integral where the subscripts on ϕ **and** ϕ^* **don't match will be zero because these wavefunctions are orthogonal and any integrals where the subscripts match will equal one because** ϕ **and** ϕ^* **are normalized. This leaves** $N^2\left(a^2 + b^2\right) = 1$ **and thus** $N = \sqrt{\dfrac{1}{a^2 + b^2}}$**.**

The normalized wavefunction is $\psi = \sqrt{\dfrac{1}{a^2 + b^2}}\left(a\phi_1 + b\phi_2\right)$**.** *Note that this is the general expression for the normalization constant of a wavefunction that is a linear combination of two orthonormal wavefunctions.*

b. (5 Points) If $\hat{H}\phi_1 = E_1\phi_1$ and $\hat{H}\phi_2 = E_2\phi_2$, determine $\langle\psi|\hat{H}|\psi\rangle$ in terms of E_1 and E_2.

$\langle\psi|\hat{H}|\psi\rangle$ **may be written as** $\langle\psi|\hat{H}|\psi\rangle = \dfrac{1}{a^2 + b^2}\langle a\phi_1 + b\phi_2|\hat{H}|a\phi_1 + b\phi_2\rangle$**, and then expanded as follows.**

$$\langle\psi|\hat{H}|\psi\rangle = \frac{1}{a^2 + b^2}\left(a^2\langle\phi_1|\hat{H}|\phi_1\rangle + ab\langle\phi_1|\hat{H}|\phi_2\rangle + ab\langle\phi_2|\hat{H}|\phi_1\rangle + b^2\langle\phi_2|\hat{H}|\phi_2\rangle\right)$$

Applying the Hamiltonian (remember it operates on the wavefunction to the right first) gives this expression $\langle\psi|\hat{H}|\psi\rangle = \dfrac{1}{a^2 + b^2}\left(a^2E_1\langle\phi_1|\phi_1\rangle + abE_2\langle\phi_1|\phi_2\rangle + abE_1\langle\phi_2|\phi_1\rangle + b^2E_2\langle\phi_2|\phi_2\rangle\right)$**.**

Since $\langle\phi_i|\phi_j\rangle = \delta_{i,j}$ **(because** ϕ_1 **and** ϕ_2 **are orthonormal),** $\langle\psi|\hat{H}|\psi\rangle = \dfrac{\left(a^2E_1 + b^2E_2\right)}{a^2 + b^2}$**.**

Note that this is the general expression for the expectation value of the energy for a wavefunction that is a linear combination of two orthonormal wavefunctions.