1. Can you imagine a case where the Hermitian nature of the Hamiltonian operator would be useful?

2. Can you imagine a way to use the variational principle in practice?

3. The variational principle allows one to choose a wavefunction that gives the lowest energy, which provides the best wavefunction in an energetic sense. This isn't the same as finding the closest wavefunction to the ground-state wavefunction (see below) but if your energy is close enough to the ground-state energy, you can be assured that the wavefunction is also very close to the ground-state wavefunction. Explain why. (Assume, for simplicity, that the ground state is nondegenerate.)

$$\min_{\Psi} \langle \Psi - \psi_0 | \Psi - \psi_0 \rangle$$

4. What are the postulates of quantum mechanics?

5. Why is it important that quantum-mechanical observables correspond to Hermitian operators?

6. What is the Heisenberg Uncertainty principle?

7. What is the variational principle?

8. List all the Hermitian operators you know.

9. What do the Dirac and Kronecker delta notations mean?

10. When is a basis set appropriate? When is perturbation theory more appropriate?

11. Consider the hydrogen molecule ion, H_2^+. Is it more sensible to use the secular equation (basis-set-expansion) or perturbation theory? What if the bond length is very small? What if the bond length is very large?

12. Show that if you minimize the energy as a function of the basis-set coefficients using the variational principle, then you obtain the secular equation.

13. If a uniform external electric field of magnitude F in the $\hat{u} = [\hat{u}_x, \hat{u}_y, \hat{u}_z]^T$ direction is applied to a particle with charge q, the potential $V(x, y, z) = -qF(u_x x + u_y y + u_z z)$ is added to the Hamiltonian. (This follows from the fact that the force applied to the particles is proportional to the electric field, $\text{force} = q\vec{E} = qF\hat{u}$ and the force is $\text{force} = -\nabla V(x, y, z)$. If the field is weak, then perturbation theory can be used, and the energy can be written as a Taylor series. The coefficients of the Taylor series give the dipole moment (μ), dipole polarizability (α), first dipole hyperpolarizability (β), second dipole hyperpolarizability (γ) in the $\hat{u}$ direction.

   o The dipole moment, μ, of any spherical system is zero. Explain why.
   o The polarizability, α, of any system is always positive. Explain why.

$$E_k(F) = E_k(0) + F \left[\frac{dE_k}{dF} \right]_{F=0} + \frac{F^2}{2!} \left[\frac{d^2 E_k}{dF^2} \right]_{F=0} + \frac{F^3}{3!} \left[\frac{d^3 E_k}{dF^3} \right]_{F=0} + \frac{F^4}{4!} \left[\frac{d^4 E_k}{dF^4} \right]_{F=0} + \cdots$$

$$= E_k(0) - F\mu_{F=0} - \frac{F^2}{2!} \alpha_{F=0} - \frac{F^3}{3!} \beta_{F=0} - \frac{F^4}{4!} \gamma_{F=0} + \cdots$$

14. The Hellmann-Feynman theorem indicates that given the ground-state wavefunction for a molecule, the force on the nuclei can be obtained. Explain how.

15. What does it mean that perturbation theory is inaccurate when the perturbation is large?

16. Can you explain why the energy goes down when the electron-in-a-box is placed in an external field?

17. For a sufficiently-highly excited state, the effect of an external electric field is negligible. Why is this true intuitively? Can you show it graphically? Can you explain it mathematically?

18. What is the secular equation?

19. What is the Hellmann-Feynman theorem?

20. How is the Hellmann-Feynman theorem related to perturbation theory?

21. What is perturbation theory? What is the expression for the first-order perturbed wavefunction?

22. To what extent is the shape of the spherical harmonic intuitive, especially the doughnut shapes associated with an electron's angular momentum around the z axis.

23. In one-electron atoms, the eigenenergies depend only on the principle quantum number, n, and not the angular momentum quantum number, l. Why are s orbitals lower in energy than p orbitals in real multielectron atoms, but not one-electron atoms? It turns out this is *not* an accidental degeneracy, but a hidden symmetry of the Hydrogen atom.

24. Suppose electrons did not repel each other. Can you write the wavefunction for a many-electron atom in that case?

25. Why do you think solving the Schrödinger equation for the one-electron molecule is more complicated than solving the Schrödinger equation for the one-electron atom?

26. For what Z is the energy of a one-electron atom comparable to the rest-mass energy of an electron, mc^2? For atomic numbers close to this value, relativistic effects become extremely important.

27. The Kratzer-Fues potential, $V_{\text{Kratzer-Fues}}(r) = \frac{a}{r^2} - \frac{b}{r}$ (here $a > 0$ and $b > 0$) is a reasonable model for a diatomic molecule rotating and vibrating in 3 dimensions, or even a ion-pair complex (e.g., an single ion pair from an ionic solvent in the gas phase). What are the solutions to the Schrödinger equation for the Kratzer-Fues potential? Solution

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{a}{r^2} - \frac{b}{r} \right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

28. What are eigenfunctions for the $n = l + 1$ state of a one-electron atom?

29. What are the energy eigenfunctions and eigenvalues for a one-electron atom? The eigenvalues should be exact, but the eigenfunctions can be qualitative.

30. How does the energy increase as the atomic number increases?

31. When will the orbital approximation be most accurate? Least accurate?

32. Explain what the Hartree-Fock approximation has to do with the concept of effective nuclear charge.

33. Can you think of a system where a single Slater determinant would be an extremely poor approximation?

34. Derive the Rydberg formula.

   o An advanced (and approximate) version of the Rydberg formula holds for highly-excited states of most atoms and molecules, and is particularly accurate for excitations from the highest occupied (ns orbital) of alkali metal atoms. The basic idea is that the excitation energy can be expressed as a formula like the below, where the quantum defect, δ_l, depends on the orbital angular momentum of the state. Can you understand where the below formula for the excitation energy comes from? Why does the quantum defect depend on angular momentum? Why does the quantum defect decrease as the angular momentum of the state? (For example, for Rubidium, $\delta_0 = 3.13$ but $\delta_2 = 1.35$.) Why does the quantum defect increase for heavier alkali metal atoms? (For example, for Li, $\delta_0 = 0.41$ but for Cs, $\delta_0 = 4.13$.)

$$\Delta E_{ns \to n'l'} \approx \frac{1}{2}\left(\frac{1}{(n-\delta_0)^2} - \frac{1}{(n'-\delta_{l'})^2}\right)$$

35. Can you derive a Rydberg-like formula for the wavenumber of excitations for a particle-in-a-box? How would this formula become more complicated for particles-in-a-box in higher dimensions?

36. For conjugated linear molecules like the cyanine dyes, the π-electrons are really confined to a 3-dimensional region, but the size of the region that is perpendicular to the conjugation is much smaller. For example, one could consider a 3-dimensional box or a 3-dimension cylinder:

$$\hat{H}_{\text{p-in-3d-box}} = -\frac{\hbar^2}{2m}\nabla^2 + V_{a_x}(x) + V_{a_y}(y) + V_{a_z}(z)$$

$$\hat{H}_{\text{p-in-cylinder}} = -\frac{\hbar^2}{2m}\nabla^2 + V_{a_z}(z) + V_{a_r}(r)$$

$$V_a(x) = \begin{cases} +\infty & x \le 0 \\ 0 & 0 < x < a \\ +\infty & a \le x \end{cases}$$

- What are the eigenfunctions and eigenenergies for these systems?
- Why is the one-dimensional particle-in-a-box model sufficient for describing the *spectroscopy* of cyanine dyes? How long does the chain need to be (e.g., for what value of k) before the non-one-dimensionality of the box becomes important? You can assume the following (reasonable-ish) values for the parameters:

$$a_x = a_y = 2 \cdot 10^{-10} \text{ m}$$
$$a_r = 1 \cdot 10^{-10} \text{ m}$$
$$a_z = (5.67 + 2.49(k+1)) \cdot 10^{-10} \text{ m} = (10.71 + 4.71(k+1)) \text{ a.u.}$$

37. The Coulomb potential governing interparticle attraction/repulsion between two particles, with charges q_m and q_n and positions $\mathbf{r}_m$ and $\mathbf{r}_n$ in a d-dimensional system is given below. Note that these expressions are *not* the usual inverse power of the distance. Nonetheless, when considering systems like the cyanine dyes or 2-dimensional quantum dots, we usually use the 3-dimensional Coulomb potential. Why?

$$V_{\text{Coulomb}} = \begin{cases} (q_m q_n)|\mathbf{r}_m - \mathbf{r}_n|^{2-d} & d > 0 \text{ and } d \neq 2 \\ (q_m q_n) \ln |\mathbf{r}_m - \mathbf{r}_n| & d = 2 \end{cases}$$

38. What are bosons? What are fermions? How do the wavefunctions differ?

39. Write the Schrödinger equation for a many-electron molecule in the Born-Oppenheimer approximation.

40. What is the fundamental assumption that underlies the orbital approximation?

41. What is a Slater determinant?

42. What is the fundamental idea behind Hartree-Fock theory?

43. How does one use the secular equation to approximate the wavefunction for a many-electron system?