Here are some questions to test your mastery of the fundamentals of approximation methods used in quantum chemistry. Once you’ve mastered the material, you should be able to answer these questions without reference to your notes or textbook.

For the variational method:

1. In general terms, what is meant by a variational principle, and how is it used to get an approximate solution to a problem?

A variational principle is in an inequality that states the lowest value of some functional is given by the exact solution to a problem. An approximate solution to a problem can then be obtained by making guesses, and choosing the one that gives the lowest value of that functional.

2. What specifically is the variational principle in quantum mechanics (as described in your text, and discussed in class)?

In quantum mechanics, a variational principle exists for the ground state energy of a system; namely the functional \( E[\phi(r)] = \int \phi^*(r) \hat{H} \phi(r) dr \) attains its lowest value when \( \phi(r) \) is the exact ground state of \( \hat{H} \).

Thus, if we were to model a given system with a wave function of our choosing, then the energy we calculate for the system will always be greater than or equal to the actual (experimentally determined) energy, and will be equal in the event that our wave function is the “true” ground state wave function. By incorporating one or more variational parameters into our wave function the corresponding energy becomes a function of these parameters, and by minimizing the energy with respect to these parameters we may determine the best form of our wave function.

3. What is a trial function, and what if any restrictions are there on the choice of trial function? E.g., does it need to be normalized? Why or why not?

A trial function is a model wave function used to approximate a system to which there may or may not be an exact solution. A trial function and its first derivative must be well-behaved, i.e. single-valued, continuous, normalizable, and finite for all values of the coordinates of the system. However, it need not be normalized because the variational functional for the energy is independent of any constant multiplying the trial function. (The normalization constant is automatically performed by the variational functional.)

4. What is a variational parameter, and how is it used? Do we always get an improved answer with additional variational parameters?

A variational parameter is a parameter upon which the trial function depends. By varying this parameter until the variational energy is minimized, the best form of the given trial
function may be found. More parameters will not always lead to a better result: for example, if the correct form of the wave function is chosen initially and more terms are added, then the result will still be the exact GS energy.

5. Can we ever get the exact answer using the variational method? When can we?

Yes: if the form of the trial function happens to be the same as the true wave function (assuming a non-degenerate ground state), then the minimized energy will be equal to the actual energy and the final function we determine will be the same as the true wave function.

6. What happens if I use an exponential function for the trial function for hydrogen?

This is a specific case of the prior question. If you were to use an exponential function, then you would obtain the exact ground state energy and ground state wave function.

7. In atomic units, what is the ground state energy of hydrogen? In atomic units, what is the first excited state energy?

The ground state energy of hydrogen is $-1/2$ Hartree, while the energy of the first excited state is $-1/8$ Hartree.

8. What is the effective nuclear charge? How does it come out from a variational calculation? Why should it be between one and two for Helium?

The effective nuclear charge is the net positive charge an electron “feels” in an atom, and will be less than the actual charge of the nucleus because electrons in the system repel one another and effectively “screen” each other from the nucleus’ full effects. By using an exponential trial function with the form of the hydrogen ground state function, we can make the nuclear charge $Z$ a variational parameter and determine it with the variational method. Since there are two protons and two electrons in Helium, each electron may “screen” anywhere from no positive charge to one positive charge, meaning the effective nuclear charge must be somewhere between one and two.

9. For a trial function that depends linearly on its variational parameters, what type of equation results from solving for the variational minimum energy?

For a trial function where the variational parameters appear as the coefficients of a linear combination of functions, a set of simultaneous linear equations in these coefficients will result. This set of equations can be solved by solving for the energies from the secular determinant.

10. What are matrix elements, and how are they calculated? Where are they used?
Matrix elements are energy and overlap terms \( H_{ij} = \int \phi_i^*(r) \hat{H} \phi_j(r) dr \) and \( S_{ij} = \int \phi_i^*(r) \phi_j(r) dr \) for a variational calculation with trial functions depending linearly on its variational parameters. They are used to find the minimum energy through their incorporation into the secular determinant and the subsequent secular equation.

In addition, you should feel comfortable doing problems like those that have been assigned in homework. Here are some additional problems you should feel comfortable doing once you’ve mastered the material.

1. Given any Hamiltonian (e.g. hydrogen, harmonic oscillator, etc.), choose a trial function with some variational parameter(s).
2. Given any Hamiltonian, and given a trial function, write down the integrals that need to be solved to get the variational energy. If the integrals are doable, solve for the variational optimum energy and the corresponding wavefunction.