Here are some questions to test your mastery of the fundamentals of the chemical bond in diatomic molecules. Once you’ve mastered the material, you should be able to answer these questions without reference to your notes or textbook.

1. In words, what is the physical idea behind the Born-Oppenheimer approximation? Which terms in the molecular Hamiltonian are dropped in the approximation?

The Born-Oppenheimer approximation assumes that nuclear motion is so slow compared to the movement of the electrons that the nuclei may be considered as being motionless relative to the electrons, and the nuclear kinetic energy terms may be neglected. The nuclear positions then become parameters in the solution of the electronic states and energies.

2. What is a molecular orbital?

A molecular orbital is a one-electron wave function for electrons in a molecule. It is often spread across several nuclei or sometimes the entire molecule.

3. Why is the internuclear distance, R, considered a parameter in solving for the electronic states?

By the Born-Oppenheimer approximation, the nuclear positions are slow moving compared to electronic motion, and can be considered parameters. For a diatomic, this corresponds to setting the internuclear distance, R, as a parameter.

4. Be able to sketch the overlap integral $S(R)$ as a function of $R$, for two 1s orbitals centered on two different nuclei a distance $R$ apart. Explain what values you physically expect for $R=0$ and $R->\infty$.

For $R=0$ the overlap integral should equal one because the orbitals share exactly the same space and are normalized. As the separation approaches infinity the integral should go to 0 since the integrand is zero for all space.

5. Be able to explain qualitatively what is the Coulomb integral.

The Coulomb integral captures the electron-electron repulsion energy of a given electron with the average charge density of another electron.

6. What is a Linear Combination of Atomic Orbitals – Molecular Orbital (LCAO-MO)? Which atomic orbitals are used, and where are they located?

An LCAO-MO is a molecular orbital constructed by linearly combining appropriate atomic orbitals centered on their respective nuclei. Any orbitals may be used which produce a net overlap, e.g. a 1s on one nucleus and a 2p, on another may not be used together because there is no net overlap. Also, only orbitals close in energy effectively
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combine to generate a MO. As mentioned in the acronym, a linear combination of these orbitals is required.

7. What are the 1s bonding and antibonding orbitals in H\textsubscript{2}^+? Be able to sketch them. Be able to normalize them, and do the usual quantum manipulations with them (calculate expectation values, operate on them with operators, etc.). Be able to evaluate the variational energy of both, in terms of \( E_{1s}, S(R), J(R), \) and \( K(R) \).

Bonding: \( \psi_b = \frac{1}{\sqrt{2(1+S)}} (1s_A + 1s_B) \)
Antibonding: \( \psi_{ab} = \frac{1}{\sqrt{2(1-S)}} (1s_A - 1s_B) \)

8. Sketch the energy of the H\textsubscript{2}^+ molecule as a function of \( R \), when the electronic state is a) the ground state \( \psi_+ \), and b) the first excited state \( \psi_- \). Indicate on the graphs where the equilibrium bond length is, and what the bond energy is.

See Fig. 9.6 in McQuarrie. The bond energy is the depth of the well in the potential.

9. In the LCAO-MO treatment of the H\textsubscript{2} molecule, what is the ground state? Why is it a determinantal wavefunction? Again, be able to sketch the molecular energy as a function of \( R \), and indicate the equilibrium bond length and bond energy.

\[ \psi_{H_2} = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) \\ \psi_\alpha(2) & \psi_\beta(2) \end{vmatrix} \]

The MO is a determinantal wave function because there is more than one electron: the wave function must reflect the fact that the electrons are indistinguishable and must also be antisymmetric.

10. What is the first excited state of the H\textsubscript{2} molecule?

\[ \psi_{H_2}^* = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_\alpha(1) & \psi_{ab}\alpha(1) \\ \psi_\alpha(2) & \psi_{ab}\alpha(2) \end{vmatrix} \]

Note that we have chosen the triplet state, as we expect it to be lower in energy than the singlet.

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. Be able to write down the Hamiltonian in SI and atomic units for each of the following: \( H_2^+, H_2, H_2^-, He_2^+ \)
2. Be able to explain briefly but mathematically why the overlap between the 1s orbital on nucleus A and either of the 2pₓ or 2pᵧ orbital on nucleus B is zero, but is nonzero with the 2p𝑧 orbital (pointing along the internuclear axis) on nucleus B.

The overlap between the 1s and say the 2pₓ orbital is zero due to symmetry: the integrand is odd with respect to x, and so the overlap integral is zero. There is no such symmetry for the case of the 2p₂ orbital.