VARIATIONS
Homework for Fri Oct 14

• Study: 21.4, 23.3
• Read: 23.4, 24.1, 24.2
Last time:

1. Screening, and coupled, self-consistent Hartree equations for many-electron atoms
2. 4\textsuperscript{th} quantum number: spin
3. Filling (auf-bau) of the periodic table
4. Physical trends on sizes, IP, EA. (e.g., why He is smaller than H)
Variational Principle

\[ E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]
Variational Principle

\[ E[\Psi] = \frac{\langle \Psi \hat{H} \Psi \rangle}{\langle \Psi \Psi \rangle} \]

\[ E[\Psi] \geq E_0 \]

If \( E[\Psi] = E_0 \), then \( \Phi \) is the ground state wavefunction, and vice versa…
Good Quantum Numbers

\[
\frac{d}{dt} \langle \hat{A} \rangle = \frac{d}{dt} \langle \Psi | \hat{A} | \Psi \rangle = \frac{1}{i\hbar} \left\langle \left[ \hat{A}, \hat{H} \right] \right\rangle
\]

If \( A \) commutes with the Hamiltonian, its expectation value does not change with time (it’s a constant of motion – if we are in an eigenstate, that quantum number will remain constant)
Atomic Units

- $m_e=1$, $e=1$, $a_0$ (Bohr radius)=1, $\hbar = 1$

\[ \varepsilon_0 = \frac{1}{4\pi} \]

Energy of 1s electron=\( -\frac{1}{2} \frac{Z^2}{n^2} \)

(1 atomic unit of energy=1 Hartree=2 Rydberg=27.21 eV)
Energy of an Hydrogen Atom

\[ E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]
Energy of an Hydrogen Atom

\[ E_\alpha = \frac{\langle \Psi_\alpha | \hat{H} | \Psi_\alpha \rangle}{\langle \Psi_\alpha | \Psi_\alpha \rangle} \]

\[ \Psi_\alpha = C \exp(-\alpha r) \]

\[ \langle \Psi_\alpha | \Psi_\alpha \rangle = \pi \frac{C^2}{\alpha^3}, \quad \langle \Psi_\alpha | -\frac{1}{2} \nabla^2 | \Psi_\alpha \rangle = \pi \frac{C^2}{2\alpha} \quad \langle \Psi_\alpha | -\frac{1}{r} | \Psi_\alpha \rangle = -\pi \frac{C^2}{\alpha^2} \]
Hydrogen Molecular Ion $\text{H}_2^+$

\[
\left[ -\frac{1}{2} \nabla^2 + \left( \frac{1}{|\vec{R}_A - \vec{R}_B|} - \frac{1}{|r - \vec{R}_A|} - \frac{1}{|r - \vec{R}_B|} \right) \right] \psi(\vec{r}) = E \psi(\vec{r})
\]
Linear Combination of Atomic Orbitals

• Most common approach to find out the ground-state solution – it allows a meaningful definition of “hybridization”, “bonding” and “anti-bonding” orbitals.

• Also known as LCAO, LCAO-MO (for molecular orbitals), or tight-binding (for solids)

• Trial wavefunction is a linear combination of atomic orbitals – the variational parameters are the coefficients:

\[ \Psi_{\text{trial}} = c_1 \Psi_{1s} \left( \vec{r} - \vec{R}_A \right) + c_2 \Psi_{1s} \left( \vec{r} - \vec{R}_B \right) \]
Linear Combination of Atomic Orbitals

\[ \Psi_{\text{trial}} = c_1 \Psi_{1s}(\vec{r} - \vec{R}_A) + c_2 \Psi_{1s}(\vec{r} - \vec{R}_B) \]
Bonding and Antibonding (I)

Image of the orbital region for LCAO molecular orbitals removed for copyright reasons.
Hydrogen Molecular Ion $\text{H}_2^+$

- Born-Oppenheimer approximation: the electron is always in the ground state corresponding to the instantaneous ionic positions