Week 6

Multi-electron Atoms and Molecules

6.1 Many-electron Atoms and Molecules

- Picking up from last time, since $Z = 2$ for helium,

$$\left.\frac{\mathrm{d}E}{\mathrm{d}\lambda}\right|_{\lambda=0} = \frac{5}{8}Z = \frac{5}{4}$$

- Additionally,

$$E_{\mathrm{He}} = -Z^2 + \frac{5}{8}Z = -4 + \frac{5}{4} = -2.75\,\mathrm{a.u.}$$

    - The first equality is the ground state energy of two-electron atoms or ions.

- Summary:

    - Zeroeth-order Perturbation Theory approximation: $E_0 = -4\,\mathrm{a.u.}$
    - First-order approximation: $E_0 + E' = -2.75\,\mathrm{a.u.}$
    - Second-order: $E_0 + E' + \frac{1}{2}E'' = -2.9077\,\mathrm{a.u.}$
    - Thirteenth-order: $-2.903\,724\,33\,\mathrm{a.u.}$

- Variational calculation of Helium:

    - Simplest: $\psi_0(12) = 1\mathrm{s}(1)1\mathrm{s}(2)$. Gives $E = -2.75\,\mathrm{a.u.}$
    - Trial ψ with one parameter: $\psi_0(1,2) = \tilde{1\mathrm{s}}(1)\tilde{1\mathrm{s}}(2)$, where $\tilde{1\mathrm{s}}(1) = \sqrt{Z^3/\pi}\mathrm{e}^{-Zr_1}$. Energy: $E = -2.8477\,\mathrm{a.u.}$

- Ionization energy.

    - Simplest approximation:

$$\begin{aligned}
\mathrm{IE} &= E_{\mathrm{He}^+} - E_{\mathrm{He}} \\
&= -2 - (-2.75) \\
&= 0.75\,\mathrm{a.u.} \\
&= 1969\,\mathrm{kJ/mol}
\end{aligned}$$

    - Exact number:

$$\begin{aligned}
\mathrm{IE} &= E_{\mathrm{He}^+} - E_{\mathrm{He}} \\
&= -2 - (-2.903\,724) \\
&= 0.9033\,\mathrm{a.u.} \\
&= 2372\,\mathrm{kJ/mol}
\end{aligned}$$

- Optimal orbitals (Hartree-Fock): Optimizing the orbitals to lower the energy as much as possible.

    - $\psi(12) = \phi(r_1)\phi(r_2)$.
    - The orbital energies converge to
      $$E_{\text{HF}} = -2.8617 \, \text{a.u.}$$

- Allow the $\psi(12)$ to move beyond a simple product of orbitals (Hylleras (1930)).

    - $\psi(r_1, r_2, r_{12}) = e^{-Zr_1}e^{-Zr_2}(1 + cr_{12})$.
    - Accounting for the electron-electron repulsion (the **electron correlation energy**) gives us an energy much better than the Hartree-Fock calculation:

      $$E = -2.8913 \, \text{a.u.}$$

    - Pekeris (1959): Did a variational calculation with 1078 parameters. Was working at IBM, who told him to do something with their newest computer that would be impressive to the world. Pekeris tackled this, and got
      $$E = -2.903\,724\,375 \, \text{a.u.}$$

    which is even more accurate than 13th order perturbation theory.

        ■ This value cannot be accurately measured to this precision in the laboaratory. Additionally, relativistic quantum mechanics (using the Dirac equation of which the Schrödinger equation is only a part) predicts a value that diverges from this one around the fifth decimal point, and this is the experimentally verifiable value.
        ■ This is important because scientists want to figure out how accurately can we account for the electron cusp.

- To summarize, the improvement tiers are

    1. H orbitals.
    2. MO picture (Hartree-Fock).
    3. Solution of the Schrödinger equation (electron correlation).

- Recall that the electron has spin (from the Stern-Gerlach and Uhlenbeck-Goudsmit experiments).

    - This is analogous to orbital angular momentum:
      $$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm} \qquad\qquad \hat{L}_z Y_{lm} = m\hbar Y_{lm}$$

    - These two operators give rise to
      $$\hat{S}^2 \sigma = s(s+1)\hbar^2 \sigma \qquad\qquad \hat{S}_z \sigma = m_s \hbar \sigma$$

    where σ is the spin eigenfunction, s is the total spin angular momentum quantum number, and m_s is the spin quantum number.
    - We have $\sigma = \alpha$ or $\sigma = \beta$ where α represents "up" and β represents "down."
    - $m_s = \pm 1/2$ where $s = 1/2$, so $m_s = -s, s$.
    - Spin eigenfunctions are orthonormal, i.e.,

      $$\int \alpha^* \alpha = \int \beta^* \beta = 1 \qquad\qquad \int \alpha^* \beta = \int \beta^* \alpha = 0$$

    - Hence, each electron has four degrees of freedom (three spatial and one spin).
    - This gives rise to a **spin orbital** $\psi(x, y, z, \sigma) = \phi(x, y, z)\sigma$, which is the product of the spin and spatial orbitals.

- In fact, our ability to calculate the energy of the helium atom was complete luck — we cannot calculate the energy of any other element on the periodic table without accounting for spin.

6.2 Many-electron Atoms and Molecules / Spin

11/3:
- **Spin orbital**: A spatial orbital augmented with a spin eigenfunction. *Given by*
$$\psi(x, y, z, \sigma) = \phi(x, y, z)\sigma$$

- Key idea: Electrons are indistinguishable, i.e., if $\psi(1, 2, \ldots, N)$ where each number represents the three spatial coordinates of an electron, the N electrons in ψ must be indistinguishable.

- There are two possible ways to achieve *mathematical* indistinguishability.

    1. We can require that
    $$\psi(1, 2, 3, \ldots, N) = \psi(2, 1, 3, \ldots, N)$$
        – Essentially, this is a symmetric permutation of all pairs of particles.
    2. We can alternatively require that
    $$\psi(1, 2, 3, \ldots, N) = -\psi(2, 1, 3, \ldots, N)$$
        – Because the probability is invariant to the sign (think about taking the modulus squared and how that eliminates sign considerations).
        – Essentially, this is an antisymmetric permutation of all pairs of particles.

- Experimental observation shows two types of particles in nature.

    1. Bozons (symmetric permutations).
    2. Fermions (antisymmetric permutations).

- Electrons are Fermions.

- Prob $= \psi^*(1, 2, \ldots, N)\psi(1, 2, \ldots, N)$ tells us the probability of finding the N electrons at the positions specified by 1 through N.

- Example (helium):

    – We had $\psi(1, 2) = 1s\alpha(1)1s\beta(2)$.
    – But since the electrons are distinguishable here, we have to make them indistinguishable by letting
    $$\psi(1, 2) = 1s\alpha(1)12\beta(2) - 1s\alpha(2)1s\beta(1)$$
    $$= 1s(1)1s(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$
        ■ Here, we've separated out the spatial and spin parts.

- How to represent antisymmetry.

    – Grassmann Wedge Product (1850s): Herman de Grassmann was studying linear algebra and would learn about higher dimensional spaces in his dreams.
    – de Grassman says
    $$\psi(1, 2) = 1s\alpha(1) \wedge 1s\beta(2)$$
    $$\frac{1}{2!}(1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1))$$
    where $\wedge$ is the wedge product, a tensor product.
        ■ We can normalize the above by substituting $\sqrt{2!}$ for 2!.
    – Slater determinant (1930): Took
    $$\psi(1, 2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

- We now consider lithium.

  - Let's put 3 electrons in a single orbital:

  $$\psi(1,2,3) = 1s\alpha(1) \wedge 1s\beta(2) \wedge 1s\beta(3)$$

    ■ $1s\beta(2) \wedge 1s\beta(3)$ will vanish as per Grassmann algebra since the electrons have the same spin state. In general, $\phi \wedge \phi = 0$.

  - Thus, in general,

  $$\psi(1,2,3) = \sqrt{3!}(1s\alpha(1) \wedge 1s\beta(2) \wedge 2s\alpha(3))$$

  or, using the Slater determinant,

  $$\psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

- **Pauli exclusion principle**: Each electron must occupy a distinct spin orbital, that is, it must have a distinct set of 4 quantum numbers n, l, m, m_s.

  - Emerges naturally from the quantum mechanics as per the above.

- What if electrons were bozons?

  - Then

  $$\psi(1,2,3) = 1s\alpha(1) \vee 1s\beta(2) \vee 2s\alpha(3)$$

  where $\vee$ is the bozonic operator, i.e., the symmetric wedge product, which denotes the positive sum of all permutations.

  - We have

  $$\phi(1) \vee \phi(2) = \phi(1)\phi(2) + \phi(2)\phi(1)$$
  $$= 2\phi(1)\phi(2)$$

  - Thus, we could put an infinite number of electrons in the same orbital (all electrons could occupy the same orbital) if electrons were bozons, and our shell structure would disintegrate.

    ■ Everything would also merge; we could not form matter as we know it.

- Sodium atoms are bozons.

6.3 Chapter 8: Multielectron Atoms

From McQuarrie and Simon (1997).

11/7:
- **Atomic units**: A system of units widely adopted for atomic and molecular calculations to simplify the equations.

Property	Atomic unit	SI Equivalent
mass	mass of an electron, m_e	9.1094×10^{-31} kg
charge	charge on a proton, e	1.6022×10^{-19} C
angular momentum	reduced Planck constant, $\hbar$	1.0546×10^{-34} J s
distance	Bohr radius, $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	5.2918×10^{-11} m
energy	$e^2/4\pi\epsilon_0 a_0 = E_\mathrm{h}$	4.3597×10^{-18} J
permittivity	$4\pi\epsilon_0$	1.1127×10^{-10} C^2 J^{-1} m^{-1}

Table 6.1: Atomic units and their SI equivalents.

- **Hartree**: The atomic unit of energy. *Denoted by E_{h}.*

  – Note that in atomic units, the ground-state energy of a hydrogen atom (in the fixed nucleus approximation) is $-E_{\mathrm{h}}/2$.

- Another good reason to use atomic units is that we are still refining the values of m_e, e, $\hbar$, etc., so results computed in atomic units will hold even as these constants evolve.

- Both perturbation theory and the variational method can yield excellent results for helium.

- **Slater orbital**[1]: An orbital of the following form. *Denoted by $S_{nlm}(r, \theta, \phi)$. Given by*

$$S_{nlm}(r, \theta, \phi) = N_{nl} r^{n-1} e^{-\zeta r} Y_l^m(\theta, \phi)^{[2]}$$

  where $N_{nl} = (2\zeta)^{n+1/2}/\sqrt{(2n)!}$ and the $Y_l^m(\theta, \phi)$ are the spherical harmonics.

  – The parameter ζ is arbitrary, i.e., not necessarily Z/n as in hydrogenlike orbitals.

  – The radial components of the Slater orbitals do not have nodes like the hydrogenlike orbitals.

- **Orbital**: A one-electron wave function.

- **Hartree-Fock limit**: The best value of the energy that can be obtained using a trial function of the form of a product of orbitals.

- As such, it is advantageous to generalize our trial wave functions past simple products of orbitals.

  – Better wave functions typically include the interelectronic distance.

- This realization led scientists to abandon the orbital concept altogether in favor of finding Hartree-Fock orbitals (because they are still a useful model) and correcting them using an approach such as perturbation theory.

- Self-consistent field method for finding the Hartree-Fock orbitals (of helium).

  – Write $\psi(\mathbf{r}_1, \mathbf{r}_2)$ as a product of orbitals $\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$.

  – It follows that the potential energy that electron 1 experiences at point $\mathbf{r}_1$ due to electron 2 is

$$V_1^{\mathrm{eff}}(\mathbf{r}_1) = \int \phi^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi(\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_2$$

  where the superscript "eff" emphasizes that $V_1^{\mathrm{eff}}(\mathbf{r}_1)$ is an effective, or average, potential.

  – This allows us to define the effective one-electron Hamiltonian for electron 1 by

$$\hat{H}_1^{\mathrm{eff}}(\mathbf{r}_1) = -\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + V_1^{\mathrm{eff}}(\mathbf{r}_1)$$

  – Using this Hamiltonian and the corresponding Schrödinger equation, we can determine $\phi(\mathbf{r}_1)$, given an estimate for $\phi(\mathbf{r}_2)$. Since there is analogous Schrödinger equation for $\phi(\mathbf{r}_2)$, the self-consistent field method consists of starting with a guess for $\phi(\mathbf{r}_2)$, calculating from that $\phi(\mathbf{r}_1)$, calculating from that a better guess for $\phi(\mathbf{r}_2)$, and so on and so forth until the two wave equations are reasonably close, or **self-consistent**.

  – In practice, linear combinations of Slater orbitals are used for each $\phi(\searrow)$.

- **Uncorrelated** (electrons): A set of electrons that are taken to be independent of each other, or at least to interact only through some average (or effective) potential.

  – Uncorrelated electrons occupy mathematically separable orbitals, as in $\psi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$.

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[1]First introduced by American physicist John Slater in the 1930s.
[2]ζ is the Greek "zeta."

- **Correlation energy**: The difference between the exact energy and the Hartree-Fock approximation energy. *Denoted by* **CE**.

- **Spin quantum number**: The fourth quantum number, which represents the z-component of the electron spin angular momentum. *Denoted by* $\boldsymbol{m_s}$. *Given by*

$$m_s = \pm\frac{1}{2} \text{ a.u.}$$

  - Uhlenbeck and Goudsmit first suggested in 1925 that electrons behave like spinning tops having z-components of spin angular momentum $\pm\hbar/2$ to explain the phenomena of sodium having a doublet in its atomic spectrum where quantum theory predicts it should have a singlet.

- We graft spin onto quantum theory in an ad hoc manner here. This will suit our purposes.

  - Note, however, that Dirac developed in the 1930s a relativistic extension of quantum mechanics in which spin arises in a perfectly natural way.

- As part of this grafting, we *define* the **spin operators** $\hat{S}^2$ and $\hat{S}_z$ in an analogous manner to how we defined the angular momentum operators $\hat{L}^2$ and $\hat{L}_z$, except that we introduce half-integral angular momentum for electron spin: Indeed, let

$$\hat{S}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha \qquad\qquad \hat{S}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\beta$$

and let

$$\hat{S}_z\alpha = m_s\alpha = \frac{1}{2}\hbar\alpha \qquad\qquad \hat{S}_z\beta = m_2\beta = -\frac{1}{2}\hbar\beta$$

  - We can formally associate $\alpha = Y_{1/2}^{1/2}$ and $\beta = Y_{1/2}^{-1/2}$ in analogy with $\hat{L}^2$ and $\hat{L}_z$, but we do not have to.

  - To continue the analogy, we can actually say that the square of the *spin* angular momentum is $S^2 = \hbar^2 s(s+1)$, where $s = \pm 1/2$.

  - Since s cannot assume large values like l and thus cannot approach a classical limit, spin is strictly nonclassical.

- **Spin eigenfunctions**: The functions α and β.

- The spin operators are Hermitian, so α, β are orthonormal.

  - Formally,

$$\int \alpha^*(\sigma)\alpha(\sigma)\,\mathrm{d}\sigma = \int \beta^*(\sigma)\beta(\sigma)\,\mathrm{d}\sigma = 1$$
$$\int \alpha^*(\sigma)\beta(\sigma)\,\mathrm{d}\sigma = \int \beta^*(\sigma)\alpha(\sigma)\,\mathrm{d}\sigma = 0$$

    where σ is the **spin variable**, an object with no classical analog.

- We now include the spin function with the spatial wave function and postulate that the two are independent so that one of the following two cases holds.

$$\psi(x,y,z,\sigma) = \psi(x,y,z)\alpha(\sigma) \qquad\qquad \psi(x,y,z,\sigma) = \psi(x,y,z)\beta(\sigma)$$

- **Spin orbital**: The complete one-electron wave function ψ dependent on x, y, z, σ.

- For example, the first two spin orbitals of a hydrogenlike atom are

$$\psi_{100\frac{1}{2}} = \sqrt{\frac{Z^3}{\pi}}\mathrm{e}^{-Zr}\alpha \qquad\qquad \psi_{100-\frac{1}{2}} = \sqrt{\frac{Z^3}{\pi}}\mathrm{e}^{-Zr}\beta$$

– Note that these orbitals are orthonormal since

$$\int \psi^*_{100\frac{1}{2}}(\mathbf{r},\sigma)\psi_{100\frac{1}{2}}(\mathbf{r},\sigma)4\pi r^2\,\mathrm{d}r\,\mathrm{d}\sigma = \int_0^\infty \frac{Z^3}{\pi}\mathrm{e}^{-2Zr}4\pi r^2\,\mathrm{d}r\int \alpha^*\alpha\,\mathrm{d}\sigma = 1$$

and similarly for $\psi_{100-\frac{1}{2}}$, and since

$$\int \psi^*_{100\frac{1}{2}}(\mathbf{r},\sigma)\psi_{100-\frac{1}{2}}(\mathbf{r},\sigma)4\pi r^2\,\mathrm{d}r\,\mathrm{d}\sigma = \int_0^\infty \frac{Z^3}{\pi}\mathrm{e}^{-2Zr}4\pi r^2\,\mathrm{d}r\int \alpha^*\beta\,\mathrm{d}\sigma = 0$$

- **Pauli Exclusion Principle** (elementary): No two electrons in an atom can have the same values of all four quantum numbers.

- Consider the helium atom.

  – Let $\psi(1,2) = 1s\alpha(1)1s\beta(2)$ where $1s\alpha$ and $1s\beta$ represent $\psi_{100\frac{1}{2}}$ and $\psi_{100-\frac{1}{2}}$, respectively, and 1 and 2 represent all four coordinates (3 spatial plus 1 spin) of electrons 1 and 2, respectively.
  – Similarly, $\psi(2,1) = 1s\alpha(2)1s\beta(1)$.
  – Since no known experiment can distinguish one electron from another, $\psi(1,2) = \psi(2,1)$.
  – Formally, we must consider the two possible states

$$\psi_1 = \psi(1,2) + \psi(2,1) \qquad\qquad \psi_2 = \psi(1,2) - \psi(2,1)$$

  of two indistinguishable electrons.
  – Experimentally, ψ_2 describes the ground state of helium since $\psi_2(1,2) = -\psi_2(2,1)$, so ψ_2 is **antisymmetric**.
  – Note that the normalization constant of ψ_2 is $1/\sqrt{2}$.

- **Antisymmetric wave function**: A wave function that changes sign when two electrons are interchanged.

- The importance of antisymmetry is captured by the following more fundamental statement of the Pauli Exclusion Principle.

  Postulate 6. *All electronic wave functions must be antisymmetric under the interchange of any two electrons.*

- We were able to ignore spin in previous treatments of helium since ψ_2 can be factored into a spatial and a spin part, and any contributions from spin cancel under a Hamiltonian that does not contain any spin operators.

  – Note that factorization of $\psi^*\hat{H}\psi$ and $\psi^*\psi$ does not occur in general, but does occur for two-electron systems.

- **Determinantal wave function**: A wave function given by the determinant of a matrix whose entries are individual spin orbitals.

  – Since the determinant representation changes signs when two rows are interchanged (representing interchanging two electrons) and is equal to zero under repeated rows/columns (representing multiple electrons in the same spin orbital), the determinant representation is antisymmetric and satisfies the Pauli Exclusion Principle, respectively.

- **Normalized N-electron determinantal wave function**: The normalized determinantal wave function

$$\psi(1,\ldots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} u_1(1) & \cdots & u_N(1) \\ \vdots & \ddots & \vdots \\ u_1(N) & \cdots & u_N(N) \end{vmatrix}$$

where the u's are orthonormal spin orbitals.

- **Fock operator**: The more general effective Hamiltonian operator used for self-consistent field solutions to systems more complex than helium. *Denoted by* $\hat{\boldsymbol{F}}_{\boldsymbol{i}}$.

- **Hartree-Fock orbital**: An eigenfunction of the Fock operator. *Denoted by* $\boldsymbol{\phi}_{\boldsymbol{i}}$.

- **Orbital energy**: An eigenvalue of the Fock operator. *Denoted by* $\boldsymbol{\epsilon}_{\boldsymbol{i}}$.
    - Alternatively, the energy of a Hartree-Fock orbital.
    - ϵ_i approximates the ionization energy of an electron from the ith orbital.