

# Lecture 19

## Many-electron Atoms

### Study Goal of This Lecture

- The Hartree-Fock self-consistent field method
- Electron configuration and the periodic table
- Atomic terms

### 19.1 Preface

We further examine the many-electron states of atoms. The focus would be on the many-electron wavefunction constructed from Slater determinant of atomic orbitals. Basically, so far we have learned to construct many-electron wavefunction from single-electron spin orbitals. The next is how to solve Schrödinger equation in this limit and how to label proper many-electron wavefunction.

### 19.2 The Hartree-Fock Self-Consistent Field Method(HF-SCF)

Hartree and later Fock developed a systematic way to calculate variational wavefunction for many electron systems. The key idea is a mean field treatment and SCF procedure. We will illustrate the general idea here, but more concrete content will be handled in slide.

For a many electron atom, the Hamiltonian is:

$4\pi\epsilon_0$  omitted.

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{r_i}}_{\text{single electron operator}} + \underbrace{\sum_{i=1}^{n-1} \sum_{j=i+1}^n \frac{e^2}{r_{ij}}}_{\text{two electron operator}}. \quad (19.1)$$

Hatree assumes a product state wavefunction

$$\Phi = g(r_1, \theta_1, \phi_1)g(r_2, \theta_2, \phi_2) \cdots g(r_n, \theta_n, \phi_n), \quad (19.2)$$

where the single electron wavefunction(orbital) is

$$g(r_i, \theta_i, \phi_i) = h_i(r_i)Y_l^{m_i}(\theta_i, \phi_i). \quad (19.3)$$

The key difficulty is, of course, the electron repulsion term. Let's consider its effect on electron 1:

$$\begin{aligned} & \langle g_1 g_2 \cdots g_n | \sum_{j=2}^n \frac{e^2}{r_{1j}} | g_1 g_2 \cdots g_n \rangle \\ &= \sum_{j=2}^n \underbrace{\langle g_2 \cdots g_{j-1} g_{j+1} \cdots g_n | g_2 \cdots g_{j-1} g_{j+1} \cdots g_n \rangle}_{=1} \times \langle g_1 g_j | \frac{e^2}{r_{1j}} | g_1 g_j \rangle \\ &= \sum_{j=2}^n \iint |g_1|^2 |g_j|^2 \frac{e^2}{r_{1j}} d\tau_1 d\tau_2 \\ &= \sum_{j=2}^n e^2 \int |g_1|^2 \underbrace{\int \frac{|g_j|^2}{r_{1j}} d\tau_2}_{\text{potential caused by electron } j} d\tau_1. \end{aligned} \quad (19.4)$$

The last equation represent the integration over  $r_1, \theta_1, \phi_1$  to get energy of electron 1 in the field of electron  $j$ . Therefore, if we define  $v_i = \sum_{j \neq i} e^2 \int \frac{|g_j|^2}{r_{ij}} d\tau_j$ , then we can rewrite the full Hamiltonian into

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{r_i} + \sum_i v_i(r_i). \quad (19.5)$$

By the symmetric of the problem,  $v_i(r_i)$  is a spherically symmetric function  $\rightarrow$  independent of  $\theta_i, \phi_i$ . Thus

$$\hat{H} = \sum_i \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + v_i(r_i) \right] \equiv \sum_i \hat{h}_i. \quad (19.6)$$

This is a “mean-field” approach, notice that  $v_i(r_i)$  depends on single-electron wavefunctions  $g_j$  for all  $j \neq i$ . i.e. contains what we want to solve. So far, we only rearrange the Hamiltonian. However, now it “looks” like a sum of independent Hamiltonians. We want to solve

$$\hat{h}_i g_i = \epsilon_i g_i. \quad (19.7)$$

This can be solved using a self-consistent field approach:

1. Obtain initial guess for all  $g_1, g_2, \dots$
2. Variationally find optimal  $g_1$ , with  $g_2, g_3, \dots, g_n$  fixed.
3. Move to find  $g_2$  with  $g_1, g_3, \dots, g_n$  fixed, and continue until  $g_n$  is optimal too.
4. Goto step 2 until converged (i.e. can't lower the energy any more.)

After Hartree first use this approach to find ground state energy for atoms using a Hartree product wavefunction, Fock pointed out in 1930 that antisymmetric wavefunctions based on Slater determinants should be used for the trial wavefunctions to ensure the result satisfy the Pauli exclusion principle. Therefore, Hatree-Fock SCF method:

- Find a variational many-electron ground state wavefunction in the form of a Slater determinant.
- The procedure optimizes the single electron wavefunctions based on a mean-field assumption.
- Yields the optimal set of “orbitals”.

The Hartree-Fock approach has been applied to find accurate wavefunctions for all atoms. → Atomic electron configuration.(See Table 10.3 in Silbey.) We skip the Aufbau principle, one should see the textbook for a brief review.

### 19.3 Atomic Terms

To specify the “spin” states of the many-electron wavefunction, it is necessary to define the atomic term symbol:

$$^{2S+1}L_J$$

$L$ : Orbital angular momentum

$J$ : Total angular momentum

$2S + 1$ : Spin-multiplicity

To assign  $L, S, 2S + 1$ , the trick is to find projection on  $z$  from all spin and orbital angular momentum for all electrons and spin.

$$m_i \leftarrow l_z \text{ for electron } i$$

$$m_{s_i} \leftarrow s_z \text{ for electron } i$$

Then find all possible  $M_L, M_S, M_J$

$$L = l_1 + l_2 + \dots$$

$$S = s_1 + s_2 + \dots$$

$$J = L + S$$

Then one can determine  $L, S$  and  $J$  and write down term symbol. (See Slide for more contents.)