

PHY 742 Quantum Mechanics II

1-1:50 AM MWF via video link:

<https://wakeforest-university.zoom.us/my/natalie.holzwarth>

Plan for Lecture 29

Hartree-Fock approximation; specifically applied to the analysis of a multi electron atom

This material is not explicitly treated in your textbook, but does build on what we learned in Chapter 10.

- 1. Review and motivation**
- 2. The Hartree-Fock analysis**
- 3. Hartree-Fock analysis specifically for an atom**

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This topic is not explicitly covered in your textbook. There are quite a few sources on the internet and I will try to suggest a few as well. The Hartree-Fock method is a venerable method for reasonably accurate modeling of real materials.

Topics for Quantum Mechanics II

Single particle analysis

- Single particle interacting with electromagnetic fields – EC Chap. 9
- Scattering of a particle from a spherical potential – EC Chap. 14
- More time independent perturbation methods – EC Chap. 12, 13
- Single electron states of a multi-well potential → molecules and solids – EC Chap. 2,6
- Time dependent perturbation methods – EC Chap. 15
- Relativistic effects and the Dirac Equation – EC Chap. 16
- Path integral formalism (Feynman) – EC Chap. 11.C

Multiple particle analysis

- Quantization of the electromagnetic fields – EC Chap. 17
- Photons and atoms – EC Chap. 18
- Multi particle systems; Bose and Fermi particles – EC Chap. 10
- Multi electron atoms and materials -- various internet sources
 - Hartree-Fock approximation & density functional treatment of atoms**
 - Hartree-Fock approximation & density functional treatment of molecules and solids

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In these first lectures, we will focus on treatment of an atom.

21	Mon: 03/23/2020	Chap. 17	Quantization of the Electromagnetic Field	#17	03/25/2020
22	Wed: 03/25/2020	Chap. 17	Quantization of the Electromagnetic Field	#18	03/27/2020
23	Fri: 03/27/2020	Chap. 17	Quantization of the Electromagnetic Field	#19	03/30/2020
24	Mon: 03/30/2020	Chap. 18	Photons and atoms		
25	Wed: 04/01/2020	Chap. 10	Multiparticle systems	#20	04/03/2020
26	Fri: 04/03/2020	Chap. 10	Multiparticle systems	#21	04/06/2020
27	Mon: 04/06/2020	Chap. 10	Multielectron atoms	#22	04/08/2020
28	Wed: 04/08/2020	Chap. 10	Multielectron atoms		
	Fri: 04/10/2020	No class	<i>Good Friday</i>		
29	Mon: 04/13/2020	Chap. 10	Multielectron atoms	#23	04/15/2020
30	Wed: 04/15/2020				
31	Fri: 04/17/2020				
32	Mon: 04/20/2020				
33	Wed: 04/22/2020				
34	Fri: 04/24/2020				
35	Mon: 04/27/2020				
36	Wed: 04/29/2020		Review		

The homework problem for this lecture involves evaluating some of the integrals we have been discussing

Review and motivation

General considerations in the study of multiple electron systems

- **The wave function for the multiple electron system should take into account the properties of indistinguishable Fermi particles**
- **The particular systems that we would like to model (atoms, molecules, solids...) also generally have both electronic coordinates as well as nuclear coordinates. For the moment, we will neglect the nuclear coordinates and just focus on the electron behaviors**
- **Special tricks have been developed for the treatments of atoms, diatomic molecules, more complicated molecules, and extended systems (solids). In general, simple systems can be treated in greater detail/accuracy than can more complicated systems. For example, consider the detailed atomic spectroscopy studied for all of the atoms in the periodic table**

Example from the NIST website

NIST Atomic Spectra Database Levels Data

Fe I 847 Levels Found
 Z = 26, Fe isoelectronic sequence

Configuration	Term	J	Level (eV)
3d ⁶ 4s ²	a ⁵ D	4	0.0000000
		3	0.05156912
		2	0.08728574
		1	0.11011433
		0	0.12126572
3d ⁷ (⁴ F)4s	a ⁵ F	5	0.85899575
		4	0.91460216
		3	0.95815732
		2	0.99011114
		1	1.01105567
3d ⁷ (⁴ F)4s	a ³ F	4	1.48486438
		3	1.55735732
		2	1.60789576
3d ⁷ (⁴ P)4s	a ⁵ P	3	2.17594511
		2	2.19786638
		1	2.22271207
3d ⁶ 4s ²	a ³ P ²	2	2.27860464
		1	2.42419829
		0	2.48437253
		0	2.48437253
3d ⁶ (⁵ D)4s4p(³ P ^o)	z ⁷ D ^o	5	2.39920469
		4	2.42543330
		3	2.44955976
		2	2.46883471
		1	2.48211838
3d ⁶ 4s ²	a ³ H	6	2.40407442
		5	2.43269468
		4	2.45343042

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Last week, we introduced the NIST Atomic Spectra Database. Here is another example – Fe which shows some of the complexity involved with transition metal materials.

Why is this important?

1. It is not really ..
2. It could be useful for testing experiment/theory
3. It could be useful for certain types of measurements
4. It may be important for atom lovers, but means nothing to the study of molecules and solids

Plan –

1. Discuss the general equations for multielectron systems
2. Discuss the Hartree-Fock treatment
3. Set up the particular equations for atoms
4. How to analyze systems beyond the Hartree-Fock approximation

Discussion points

General equations for multi electron systems

We have established that in order to represent N indistinguishable Fermi particles: the wave function must have the property:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i \dots \mathbf{r}_j \dots \mathbf{r}_N) = -\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j \dots \mathbf{r}_i \dots \mathbf{r}_N)$$

For example, we can construct a wave function that has the correct antisymmetry from combinations of single particle states $\varphi_a(\mathbf{r}), \varphi_b(\mathbf{r}), \varphi_c(\mathbf{r}) \dots$

Example for N particles using Slater determinant:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_a(\mathbf{r}_1) & \varphi_a(\mathbf{r}_2) & \varphi_a(\mathbf{r}_3) & \cdots & \varphi_a(\mathbf{r}_N) \\ \varphi_b(\mathbf{r}_1) & \varphi_b(\mathbf{r}_2) & \varphi_b(\mathbf{r}_3) & \cdots & \varphi_b(\mathbf{r}_N) \\ \varphi_c(\mathbf{r}_1) & \varphi_c(\mathbf{r}_2) & \varphi_c(\mathbf{r}_3) & \cdots & \varphi_c(\mathbf{r}_N) \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \varphi_z(\mathbf{r}_1) & \varphi_z(\mathbf{r}_2) & \varphi_z(\mathbf{r}_3) & \cdots & \varphi_z(\mathbf{r}_N) \end{vmatrix}$$

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Review of the properties of identical Fermi particles.

In general, the Hamiltonian of the system takes the form:

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N h(\mathbf{r}_i) + \frac{1}{2} \sum_{i,j=1(i \neq j)}^N v(\mathbf{r}_i, \mathbf{r}_j)$$

Here $v(\mathbf{r}_i, \mathbf{r}_j) = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ representing electron-electron repulsion

For an atom having atomic number Z , $h(\mathbf{r}_i) = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i}$

Identification of one-electron and two-electron terms.

If we choose our single particle basis as eigenstates of the single particle Hamiltonian: $h(\mathbf{r}_1)\varphi_a(\mathbf{r}_1) \equiv \varepsilon_a\varphi_a(\mathbf{r}_1)$

Second quantized version of the multi electron system:

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Rightarrow \sum_i \varepsilon_i f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Here v_{ijkl} denotes matrix elements such as

$$v_{ijkl} = \langle \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2) | v(\mathbf{r}_1 - \mathbf{r}_2) | \varphi_k(\mathbf{r}_1)\varphi_l(\mathbf{r}_2) \rangle$$

Second quantization formulation.

For the more general choice of single particle basis $\varphi_a(\mathbf{r})$:

(note the basis functions must be orthonormal: $\langle \varphi_a(\mathbf{r}) | \varphi_b(\mathbf{r}) \rangle = \delta_{ab}$)

Second quantized version of the multi electron system:

$$H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Rightarrow \sum_i h_{ii} f_i^\dagger f_i + \sum_{ijkl} v_{ijkl} f_i^\dagger f_j^\dagger f_l f_k$$

Here h_{ii} denotes single particle matrix elements

$$h_{ii} = \langle \varphi_i(\mathbf{r}) | h(\mathbf{r}) | \varphi_i(\mathbf{r}) \rangle$$

Here v_{ijkl} denotes two particle matrix elements

$$v_{ijkl} = \langle \varphi_i(\mathbf{r}_1) \varphi_j(\mathbf{r}_2) | v(\mathbf{r}_1 - \mathbf{r}_2) | \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2) \rangle$$

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In this case, the basis functions are not necessarily eigenfunctions of the single particle Hamiltonian.

**How can we estimate the ground state of our multi electron Hamiltonian?
variational approach --**

Consider a Hamiltonian H having lowest eigenvalue E_0 :

It can be shown that for any function ψ

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

Proof: The Hamiltonian has a complete set of

eigenvalues and eigenvectors: $H |\phi_i\rangle = E_i |\phi_i\rangle$

Expanding $|\psi\rangle$ in eigenvector basis: $|\psi\rangle = \sum_i C_i |\phi_i\rangle$

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_i |C_i|^2 E_i}{\sum_i |C_i|^2} \geq E_0$$

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Review of the variational principle.

Significance of this inequality --

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0$$

The inequality motivates a class of estimation methods known as variational methods to converge to the ground state energy E_0 and the corresponding ground state probability amplitude.

Define $E_{trial}(\Psi_{trial}) \equiv \frac{\langle \Psi_{trial} | H | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle}$

Minimize $E_{trial}(\Psi_{trial})$ with respect to Ψ_{trial}

The variational principle guarantees that

$$E_{trial}(\Psi_{trial}) \geq E_0$$

\Rightarrow The better the trial wavefunction, the better the estimate.

Review continued.

Hartree-Fock approximation

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MATHEMATICAL, PHYSICAL AND ENGINEERING SCIENCES

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Article

Self-consistent field, with exchange, for beryllium

Douglas Rayner Hartree and W. Hartree

Published: 01 May 1935

<https://doi.org/10.1098/rspa.1935.0085>

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Reverence to the historical paper by Hartree and Hartree

Self-Consistent Field, with Exchange, for Beryllium

By D. R. HARTREE, F.R.S., and W. HARTREE

(Received February 25, 1935)

1—INTRODUCTION

Except for the lightest atoms, most calculations of approximate wave functions and fields for many-electron atoms have been carried out by the method of the “self-consistent field,” of which the principle is, shortly, the determination of a set of one-electron wave functions such that each represents a stationary state of an electron in the field of the nucleus and the Schrödinger charge distribution of the electrons occupying the other wave functions of the set.† This method has been found quite practicable for numerical work, even for the heaviest atoms.

The Hartree-Fock approximation is based on the choice of

$$|\Psi_{trial}\rangle = \prod_{i=1}^N f_i^\dagger |0\rangle$$

using the second quantized notation or

the equivalent Slater determinant based on the single particle functions $\varphi_i(\mathbf{r})$

with the constraint $\langle \varphi_i(\mathbf{r}) | \varphi_j(\mathbf{r}) \rangle = \delta_{ij}$

$$E_{trial} = \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{i,j=1}^N (v_{ijij} - v_{ijji})$$

Note that the $i=j$ contribution cancels out.

Second quantization formulation

Matrix elements

$$h_{ii} = \int d^3r h(\mathbf{r}) |\varphi_i(\mathbf{r})|^2$$

$$v_{ijij} = e^2 \int d^3r \int d^3r' \frac{|\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

$$v_{ijji} = e^2 \delta_{\sigma_i \sigma_j} \int d^3r \int d^3r' \frac{(\varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r})) (\varphi_i^*(\mathbf{r}') \varphi_j(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|}$$

Constrained optimization

$$\delta \left(E_{\text{trial}}(\{\varphi_i\}) - \sum_{i,j=1}^N \lambda_{ij} \langle \varphi_i | \varphi_j \rangle \right) = 0$$

$$\varphi_i \rightarrow \varphi_i + \delta\varphi_i$$

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Writing out the integrals.

Constrained optimization

$$\delta \left(E_{\text{trial}}(\{\varphi_i\}) - \sum_{i,j=1}^N \lambda_{ij} \langle \varphi_i | \varphi_j \rangle \right) = 0$$

$$\varphi_i \rightarrow \varphi_i + \delta\varphi_i$$



Lagrange multiplier

Equations to solve:

$$\frac{\delta E_{\text{trial}}}{\delta \varphi_i^*} = H_{\text{eff}}(\mathbf{r})\varphi_i(\mathbf{r}) = \lambda_{ii}\varphi_i(\mathbf{r})$$

$$H_{\text{eff}}(\mathbf{r}) = h(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{Exchange}}(\mathbf{r})$$

When these equations are used to find the ground state, we note that

$$\sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 = n(\mathbf{r}) \quad \text{electron density}$$

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Equations resulting from orbital optimization.

Hartree-Fock equations to solve

$$H_{eff}(\mathbf{r})\varphi_i(\mathbf{r}) = \lambda_{ii}\varphi_i(\mathbf{r})$$

$$H_{eff}(\mathbf{r}) = h(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{Exchange}(\mathbf{r})$$

$$V_{Hartree}(\mathbf{r}) = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

In Hartree-Fock theory, the Fock contribution is actually an integral form:

$$V_{Exchange}(\mathbf{r})\varphi_i(\mathbf{r}) = -e^2 \sum_{j=1}^N \delta_{\sigma_i\sigma_j} \int d^3r' \frac{(\varphi_i(\mathbf{r}')\varphi_j^*(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} \varphi_j(\mathbf{r})$$

Simplified structure of equations.

Self-consistent solution of the Hartree-Fock equations

Guess one electron functions $\{\varphi_i(\mathbf{r})\}^0$

Count=0

Solve differential integral equations

$$H_{eff}(\mathbf{r})\varphi_i(\mathbf{r}) = \lambda_{ii}\varphi_i(\mathbf{r}) \quad \Rightarrow \{\varphi_i(\mathbf{r})\}^{new}$$

Count=Count+1

$$\{\varphi_i(\mathbf{r})\}^{Count} = \alpha\{\varphi_i(\mathbf{r})\}^{Count-1} + (1-\alpha)\{\varphi_i(\mathbf{r})\}^{new}$$

$$\text{test: if } \left| \{\varphi_i(\mathbf{r})\}^{Count-1} - \{\varphi_i(\mathbf{r})\}^{Count} \right| > \epsilon$$

$$\text{if } \left| \{\varphi_i(\mathbf{r})\}^{Count-1} - \{\varphi_i(\mathbf{r})\}^{Count} \right| < \epsilon$$



Continue self-consistent Iterations



Self-consistent cycles converged

Iteration process in order to achieve self-consistency.

4 $1s^0$

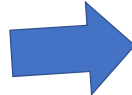
Be

Beryllium

9.0122

$1s^2 2s^2$

9.3227



PERIODIC TABLE

Atomic Properties of the Elements

NIST National Institute of Standards and Technology
U.S. Department of Commerce

18 VIIIA

Physical Measurement Laboratory www.nist.gov
Standard Reference Data www.nist.gov

2 He

FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS¹

¹ Based on 19 100 021 701 atoms of radium corresponding to the position between the two hyperfine levels of the ground state of ²²³Rn

Avogadro constant N_A 6.022 140 76 × 10²³ mol⁻¹ (exact)

Boltzmann constant k 1.380 658 529 × 10⁻²³ J K⁻¹ (exact)

Planck constant h 6.626 070 15 × 10⁻³⁴ J s (exact)

elementary charge e 1.602 176 634 × 10⁻¹⁹ C (exact)

gas constant R 8.314 472 J K⁻¹ mol⁻¹ (exact)

Ampere constant k_A 6.022 140 76 × 10²³ mol⁻¹ (exact)

Stefan-Boltzmann constant σ 5.670 373 × 10⁻⁸ W m⁻² K⁻⁴ (exact)

Boltzmann constant k_B 1.380 658 529 × 10⁻²³ J K⁻¹ (exact)

electron volt eV 1.602 176 634 × 10⁻¹⁹ J (exact)

Rydberg constant R_∞ 1.097 373 157 × 10⁷ m⁻¹ (exact)

proton mass m_p 1.672 621 923 × 10⁻²⁷ kg

neutron mass m_n 1.674 927 498 × 10⁻²⁷ kg

energy equivalent $m_e c^2$ 0.510 998 9461 MeV

fine structure constant α 7.297 352 569 × 10⁻³

hydrogen energy E_H 13.605 693 123 eV

neutronron constant of gravitation G 6.674 × 10⁻¹¹ m³ kg⁻¹ s⁻²

For the most accurate values of these and other constants, visit www.nist.gov/constants.

Solids
 Liquids
 Gases
 Artificially Prepared

13 IIIA 14 IVA 15 VA 16 VIA 17 VIIA 18 VIIIA
 5 B Boron 6 C Carbon 7 N Nitrogen 8 O Oxygen 9 F Fluorine 10 Ne Neon
 11 Na Sodium 12 Mg Magnesium 13 Al Aluminum 14 Si Silicon 15 P Phosphorus 16 S Sulfur 17 Cl Chlorine 18 Ar Argon
 19 K Potassium 20 Ca Calcium 21 Sc Scandium 22 Ti Titanium 23 V Vanadium 24 Cr Chromium 25 Mn Manganese 26 Fe Iron 27 Co Cobalt 28 Ni Nickel 29 Cu Copper 30 Zn Zinc 31 Ga Gallium 32 Ge Germanium 33 As Arsenic 34 Se Selenium 35 Br Bromine 36 Kr Krypton
 37 Rb Rubidium 38 Sr Strontium 39 Y Yttrium 40 Zr Zirconium 41 Nb Niobium 42 Mo Molybdenum 43 Tc Technetium 44 Ru Ruthenium 45 Rh Rhodium 46 Pd Palladium 47 Ag Silver 48 Cd Cadmium 49 In Indium 50 Sn Tin 51 Sb Antimony 52 Te Tellurium 53 I Iodine 54 Xe Xenon
 55 Cs Cesium 56 Ba Barium 57 La Lanthanum 58 Ce Cerium 59 Pr Praseodymium 60 Nd Neodymium 61 Pm Promethium 62 Sm Samarium 63 Eu Europium 64 Gd Gadolinium 65 Tb Terbium 66 Dy Dysprosium 67 Ho Holmium 68 Er Erbium 69 Tm Thulium 70 Yb Ytterbium 71 Lu Lutetium
 87 Fr Francium 88 Ra Radium 89 Ac Actinium 90 Th Thorium 91 Pa Protactinium 92 U Uranium 93 Np Neptunium 94 Pu Plutonium 95 Am Americium 96 Cm Curium 97 Bk Berkelium 98 Cf Californium 99 Es Einsteinium 100 Fm Fermium 101 Md Mendelevium 102 No Nihonium 103 Lr Lawrencium

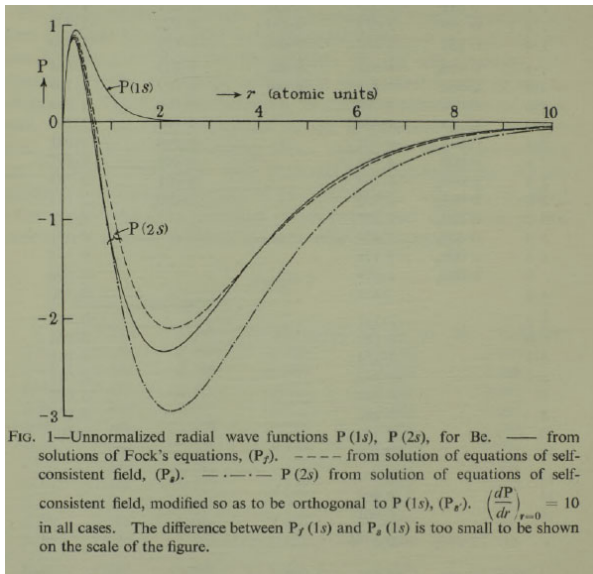
Atomic Number Ground State
 Symbol G_1
 Name Cerium
 Standard Atomic Weight A_r 140.12
 5.35058×10^{-26} kg
 6.445058×10^{-26} kg
 Ground state Configuration [Xe] 4f¹ 5d¹ 6s²
 Ionization Energy (eV) 5.5384

¹Based upon ²²³Rn; () indicates the mass number of the longest-lived isotope.

For the most precise values and uncertainties visit www.nist.gov and pmn.nist.gov/standards. NIST SP-945 (July 2019)

Details discussed in paper by Hartree and Hartree.

Example studied by Hartree and Hartree.



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Plot of radial wave functions from paper.

Other methods of solving the Hartree Fock equations

Rather than solve the coupled integral-differential radial equations, it is popular in quantum chemical contexts to represent the single particle functions as a sum of particular (fixed) basis functions. The variational parameters are then the linear coefficients of the basis functions

$$\varphi_i(\mathbf{r}) = \sum_{\alpha} C_{\alpha}^i \chi_{\alpha}(\mathbf{r})$$

Alternative method for carrying out Hartre-Fock analysis.