The Atomic Many-Body Theory course

Based on the book:

- Atomic Many-Body Theory, Lindgren and Morrison.

Other books to consult

- Atomic Structure Theory, Walter Johnsson
- Computational Atomic Structure: An MCHF Approach, Charlotte Froese-Fisher

The Atomic Many-Body Theory course

The course is divided into two parts:

Part I

- Chapter 1-4 Tensor operators and Angular Momentum Graphs
- Chapter 2 Definitions of Spherical Tensor Operators, Angular Momentum coupling, Wigner Eckarts Theorem Problem 2.1 -2.3, 2.6-2.8, 2.12-2.19
- Chapters 3 and 4 Angular Momentum Graphs All problems

More information on this part can be found in: Edmonds A. R. Angular Momentum in Quantum Mechanics, Princeton 1960.

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Part II

- Chapter 5-8, Independent Particle Model
- Chapter 9-14, Perturbation Theory
- Chapter 15 Coupled- Cluster Theory

Requirement:

- make the excersises (many in the first four chapters, then much less) .
- Look deeper into one subject and present it to the others. The subject can be chosen from Chapter 5 and onwards, and may focus on something not covered by the book. The presentation should be take around 20 minutes.

The N-body problem

one-particle in one dimension

- discretized space (grid) in n- points
- Hamiltonian $\rightarrow$ Hamiltonian matrix: $n \times n$

N-particles in three dimensions (disregarding spin for now)

- $\Psi \sim n^{N \times 3}$ $H \sim n^{N \times 3 \times 2}$
- $n = 100, N = 2 \rightarrow H \sim 10^{24}$ elements, each element 8 byte

We can use the symmetry of the atoms...

Possibility: Spherical coordinates, orbitals $\phi^i_{n,\ell,m_\ell,m_s}(r_i,\theta_i,\phi_i)$

- **S**, **L**, M_S and M_L good quantum numbers.
- Solve for particular **S** and **L**,
- Solution independent on $z-axis$ direction $\rightarrow$ M-independent
- or with field present pick M_S and M_L
- $\mathbf{L}=\sum_i \mathbf{l}_i$, use a maximum ℓ
- discretize the radial space

Example: two particles S - symmetry $\ell \leq 3 \rightarrow ss, pp, dd, ff$ (this is the partial wave expansion - are there alternatives?)

- angular space size $=4$
- radial space $n \times n$
- $\Psi \sim n \times n \times 4 \rightarrow H \sim 10^9$ or 10 Gb with $n=100$

Two-particles are thus possible, **but when the N grows we will sooner or later hit the roof**.

- a grid is simple, but expensive, and h^n-error int. & der.

Analytical Basis Sets?

- - global, infinite (where to terminate?)
- + analytical integration on the fly,
- + may converge quickly if well chosen.
- Example: hydrogen-like (-) Spherical Harmonics (+)

Primitives Basis?

- B-splines & finite elements, finite & flexible Gaussian integration, exact derivation
- DVR - often defined on Gaussian quadrature - finite base, built in boundary conditions, Gaussian integration
- Gaussians, analytical integration & derivation

From Primitive Basis to Physical Basis

Atomic or Molecular orbitals ϕ_i:

$$\phi_i = \sum_j c_{ij} B_j$$

- Why this step? We could have used the primitive basis directly...

Strategies for the Many-Body Problem

- Start with **Independent Particle model**, e.g. Hartree-Fock
- Define a zeroth order configuration (a "vacuum level")
- Expand beyond this stepwise

Configuration-Interaction, Perturbation-Theory, Coupled Cluster:

- singles, doubles, triples...

Multi-Configuration Hartree-Fock

- add configurations and vary their wave functions (instead of summing over a basis)

Strategies for the Many-Body Problem

- singles, doubles, triples...

Beryllium ground state: $4e^-\ 1s^2 2s^2$

Bunge 1976, Hartree-Fock starting point

Single excitations	0.35
Double excitations	95.22
Triple excitations	1.1
Quadruple excitations	3.4

RPA/CI singles?

CI - versus Perturbation expansion

Simple Example two *configurations*

$$\Psi = c_a|a\rangle + c_b|b\rangle \quad \left(\text{e.g.}|2s^2\rangle, |2p^2\rangle\right) \quad H\Psi = E\Psi$$

$$H = h_1 + h_2 + V_{12}, \quad (h_1 + h_2)\,|n\rangle = (\epsilon_1^n + \epsilon_2^n)\,|n\rangle$$

find c_a, c_b. If a, b, orthogonal and normalized we have

$$\begin{pmatrix} \langle a|H|a\rangle & \langle a|H|b\rangle \\ \langle b|H|a\rangle & \langle b|H|b\rangle \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = E \begin{pmatrix} c_a \\ c_b \end{pmatrix}$$

$$H_{aa} = \langle a|H|a\rangle, H_{bb} = \langle b|H|b\rangle, H_{ab} = H_{ba}^* = \langle a|H|b\rangle = \langle a|V_{12}|b\rangle$$

CI - versus Perturbation expansion

$$\begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = E \begin{pmatrix} c_a \\ c_b \end{pmatrix} \rightarrow c_b = \frac{E - H_{aa}}{H_{ab}} c_a$$

$$E^2 - E\left(H_{aa} + H_{bb}\right) - |H_{ab}|^2 + H_{aa}H_{bb} = 0$$

$$E = \frac{H_{aa} + H_{bb}}{2} \pm \sqrt{\frac{\left(H_{aa} - H_{bb}\right)^2}{4} + |H_{ab}|^2}$$

$$E = \frac{H_{aa} + H_{bb}}{2} \pm \frac{H_{aa} - H_{bb}}{2} \left(1 + \frac{4|H_{ab}|^2}{\left(H_{aa} - H_{bb}\right)^2}\right)^{1/2}$$

$$E_1 \approx H_{aa} + \frac{|H_{ab}|^2}{H_{aa} - H_{bb}} + \ldots, \quad E_2 \approx H_{bb} + \frac{|H_{ab}|^2}{H_{bb} - H_{aa}} + \ldots,$$

Converges? The levels repel each other

CI - versus Perturbation expansion

$$H_{aa} = \epsilon_1^a + \epsilon_2^a + \langle a|V_{12}|a\rangle,\ H_{bb} = \epsilon_1^b + \epsilon_2^b + \langle b|V_{12}|b\rangle \rightarrow$$

$$E_1 \approx \epsilon_1^a + \epsilon_2^a + \langle a|V_{12}|a\rangle + \frac{|\langle b|V_{12}|a\rangle|^2}{\epsilon_1^a + \epsilon_2^a - \epsilon_1^b - \epsilon_2^b} + \ldots,$$

$$E_2 \approx \epsilon_1^b + \epsilon_2^b + \langle b|V_{12}|b\rangle - \frac{|\langle b|V_{12}|a\rangle|^2}{\epsilon_1^a + \epsilon_2^a - \epsilon_1^b - \epsilon_2^b} + \ldots,$$

keeping the orders separately (here up to 2nd order only)

- $\epsilon_1^a + \epsilon_2^a < \epsilon_1^b + \epsilon_2^b \rightarrow$ 3:rd term *decrease/increase* the energy for E_1/E_2
- perturbation expansion converges $\rightarrow$ the results are identical
- just one of the states interesting? pert. theory is cheaper
- there are also diagonalizers aiming for lowest energy states (Lanzos for example)