6. HARTREE-FOCK THEORY

Independent particle approximation

Remember that the final goal is to solve the many-body Schrödinger equation

$$H|\Psi_k\rangle = E_k|\Psi_k\rangle \qquad (1)$$

The lowest-energy state $|\Psi_0\rangle$ is the ground state of the system and E_0 the ground-state energy.
H is the nuclear Hamiltonian, expressed in first quantisation as

$$H = \sum_{i=1}^{A} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j=1}^{A} V_{ij} + \dots$$

and in second quantisation as

$$H = \sum_{\alpha\beta} t_{\alpha\beta}\, a_\alpha^\dagger a_\beta + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta}\, a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta + \dots$$

An observable associated to an operator $\hat{A}$ is computed as

$$A = \langle\Psi_k|\hat{A}|\Psi_k\rangle$$

Now, the solution of equation (1) is generally quite complicated. The presence of two-body (and higher-body) operators in H introduces correlations between the different particles and implies that

$$|\Psi_i\rangle \neq \text{Slater determinants}$$

On the other hand, if particles of a many-body system are independent one has

$$H = \sum_{i=1}^{A} h_i$$

i.e. the Hamiltonian is a one-body operator only.

Then

$$H|\Psi_k\rangle = E_k|\Psi_k\rangle \longrightarrow h_i|\phi_k^i\rangle = e_k^i|\phi_k^i\rangle$$

$H|\Psi_k\rangle = E_k|\Psi_k\rangle$: A-body wave function

$h_i|\phi_k^i\rangle = e_k^i|\phi_k^i\rangle$: one-body wave function ($i = 1, \dots A$ but same equation for all i)

i.e. one goes from an A-body problem to A one-body problems, and

$$|\Psi_k\rangle \longrightarrow \prod_{i=1}^{A} |\phi_k^i\rangle .$$

Can one actually approximate $H \simeq \sum_{i=1}^{A} h_i$ in the case of nuclear systems? Does it make any sense? Is there any empirical justification?

We know that

- the interparticle distance in nuclei is about 2 fm
- the range of nuclear interactions is about 2 fm

hence, of comparable size. One would conclude that nucleons are strongly interacting and cannot be approximated as independent particles.

However

- the nucleon mean-free path is large, about 5 fm
  (it can be extracted from experiment + theoretical calculations)
- there is empirical evidence for a "shell structure" in nuclei
  (systematic deviations of measured binding energies vs. liquid-drop predictions + one-nucleon knockout experiments)

Note: <u>independent</u> particles does not mean <u>free</u> particles !
Independent particles can be under the influence of an average one-body potentials (somehow averaging the effect of interactions with all other particles).
How do we find a convenient one-body potential?

Hartree-Fock ansatz

Main idea: Find the Slater determinant $|\Phi\rangle$ that yields the best ground-state energy and approximate the exact many-body wave function $|\Psi\rangle$ by $|\Phi\rangle$

- Best ground-state energy = as close as possible to the exact energy
- Of which one-body field h the basis used to build $|\Phi\rangle$ is an eigenbasis?

- How does H influence the determination of h?
- Concretely, the way to determine the optimal $|\phi\rangle$ is through the minimisation of

$$E^{HF} \equiv \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$$

under the constraints that

i) basis functions $\{\psi_\alpha\}_{\alpha=1,\dots A}$ are orthonormal

ii) ρ is idempotent

$\downarrow$

Ritz variational principle implies that $E^{HF} \geq E_0$

i.e. E^{HF} provides an upper bound to the exact ground-state energy

- In practice: express E^{HF} in terms of the variational parameters (a_α or $\psi_\alpha(\vec{r}_1)$) and perform the minimisation

Equations of motion

First, recall that Wick's theorem applied to H with respect to $|\phi\rangle$ leads to

$$H = \underbrace{\sum_{\alpha\beta} t_{\alpha\beta}\rho_{\beta\alpha} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\bar{v}_{\alpha\beta\gamma\delta}\rho_{\gamma\alpha}\rho_{\delta\beta} + \sum_{\alpha\beta} h_{\alpha\beta} : a^\dagger_\alpha a_\beta :}_{= H_0 \text{ (zero- + one-body part)}}$$

$$+ \underbrace{\frac{1}{4}\sum_{\alpha\beta\gamma\delta} \bar{v}_{\alpha\beta\gamma\delta} : a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma :}$$

$$= H_1 \quad \text{(residual two-body part)}$$

Now, the fully contracted (= zero-body) part of H_0 is nothing else than the Hartree-Fock energy

$$E^{HF} = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \sum_{\alpha\beta} t_{\alpha\beta} \rho_{\beta\alpha} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} \bar{v}_{\alpha\beta\gamma\delta} \rho_{\gamma\alpha} \rho_{\delta\beta} \equiv E[\rho]$$

The one-body part of H_0 is instead the Hartree-Fock Hamiltonian

$$h_{\alpha\beta} \equiv t_{\alpha\beta} + U^{HF}_{\alpha\beta} = t_{\alpha\beta} + \sum_{\gamma\delta} \bar{v}_{\alpha\gamma\beta\delta} \rho_{\delta\gamma}$$

The minimisation of $E[\rho]$ under the constraint $\rho^2 = \rho$ is done via the Lagrange method with a matrix of Lagrange parameters Λ

$$\delta \left[E[\rho] - \mathrm{Tr}\left\{ \Lambda(\rho^2 - \rho) \right\} \right] = 0$$

Since the density matrix is hermitian ($\rho^*_{\mu\nu} = \rho_{\nu\mu}$) the irreducible set of independent variational parameters is

$$\rho_{\mu\nu} \text{ and } \rho^*_{\mu\nu} \qquad \text{for } \nu < \mu$$

$$\rho_{\mu\mu} \qquad \forall_\mu$$

Then, the variation of the energy yields

$$\delta E[\rho] = \sum_{\nu<\mu} \left[\frac{\delta E[\rho]}{\delta \rho_{\mu\nu}} \delta \rho_{\mu\nu} + \frac{\delta E[\rho]}{\delta \rho^*_{\mu\nu}} \delta \rho^*_{\mu\nu} \right] + \sum_{\mu} \frac{\delta E[\rho]}{\delta \rho_{\mu\mu}} \delta \rho_{\mu\mu}$$

$$= \frac{1}{2} \sum_{\mu\nu} \left[h_{\nu\mu} \delta \rho_{\mu\nu} + h^*_{\nu\mu} \delta \rho^*_{\mu\nu} \right]$$

$$= \frac{1}{2} \mathrm{Tr} \left\{ h \delta \rho + h^* \delta \rho^* \right\}$$

$$= \mathrm{Tr} \left\{ h \delta \rho \right\}$$

The variation of the constraints yields

$$\delta \mathrm{Tr} \left\{ \Lambda (\rho^2 - \rho) \right\} = \sum_{\mu\nu} \frac{\delta}{\delta \rho_{\mu\nu}} \sum_{\alpha\beta} \Lambda_{\alpha\beta} \left[\sum_{\gamma} \rho_{\beta\gamma} \rho_{\gamma\alpha} - \rho_{\beta\alpha} \right] \delta \rho_{\mu\nu}$$

$$= \mathrm{Tr} \left\{ \left(\rho\Lambda + \Lambda\rho - \Lambda \right) \delta \rho \right\}$$

Combining the two

$$\mathrm{Tr} \left\{ \left(h - \rho\Lambda - \Lambda\rho + \Lambda \right) \delta \rho \right\} = 0$$

which has to be true for an arbitrary variation $\delta\rho$, hence

$$h - \rho\Lambda - \Lambda\rho + \Lambda = 0$$

Multiplying by ρ on the left or on the right

$$\begin{cases} \rho h - \rho^2\Lambda - \rho\Lambda\rho + \rho\Lambda = 0 & (A) \\ h\rho - \rho\Lambda\rho - \Lambda\rho^2 + \Lambda\rho = 0 & (B) \end{cases}$$

$(B)-(A) \Rightarrow h\rho - \rho\Lambda\rho - \underbrace{\Lambda\rho^2}_{\text{use } \rho^2=\rho \;\leftarrow\; =\Lambda\rho} + \Lambda\rho - \rho h + \underbrace{\rho^2\Lambda}_{=\rho\Lambda} + \rho\Lambda\rho - \rho\Lambda = 0$

$\Rightarrow h\rho - \rho h = 0$

$\Leftrightarrow [h, \rho] = 0$

Therefore, the basis minimising the energy is the one that diagonalises h and ρ simultaneously.

↳ basis $\{a_\alpha\}_{\alpha=1,..\infty}$ solution of

$$h|\alpha\rangle = e_\alpha |\alpha\rangle$$

where now $e_\alpha = h_{\alpha\alpha} = t_{\alpha\alpha} + \sum_{i=1}^{A} \bar{v}_{\alpha i \alpha i}$

Comments:

- Not a standard eigenvalue problem since $h = h[\rho]$
  → iterative or "self-consistent" problem

HF potential referred to as "self-consistent potential"

- A signature of this non-linearity is already visible when computing E^{HF} in terms of the single-particle energies e_α

Naively one would expect $E^{HF} = \sum_i e_i$

where i labels the occupied states ("hole" states)

However, in the HF basis

$$\rho_{\beta\alpha} = n_\alpha \delta_{\alpha\beta}$$

↳ occupation number $= \begin{cases} 1 & \text{for holes (occupied)} \\ 0 & \text{for particles (unoccupied)} \end{cases}$

$$\Rightarrow h_{\alpha\beta} = h_{\alpha\alpha}\delta_{\alpha\beta} = e_\alpha \delta_{\alpha\beta}$$

and

$$h_{\alpha\alpha} = t_{\alpha\alpha} + \sum_i \bar{V}_{\alpha i \alpha i}$$

The HF instead reads

$$E^{HF} = \sum_i t_{ii} + \frac{1}{2}\sum_{ij} \bar{V}_{ijij}$$

$$= \sum_i t_{ii} + \sum_{ij} \bar{V}_{ijij} - \frac{1}{2}\sum_{ij} \bar{V}_{ijij}$$

$$= \sum_i e_i - \frac{1}{2}\sum_{ij} \bar{V}_{ijij} \neq \sum_i e_i$$

Solving HF equations

As mentioned, an iterative process is needed

1) One first arbitrarily chooses a set of A occupied orbitals. In practice, they should be as realistic as possible, e.g. eigenstates of a Woods-Saxon potential or harmonic oscillator potential. Let us denote the corresponding state with $|\alpha^{(0)}\rangle$

2) From these orbitals, one constructs the corresponding density matrix $\rho^{(0)}$ and computes the HF Hamiltonian

$$h^{(0)} = t + U^{(0)}$$

3) One diagonalises the HF Hamiltonian

$$h^{(0)} |\alpha\rangle = e_\alpha |\alpha\rangle$$

and obtains a new set of orbitals $|\alpha^{(1)}\rangle$ with corresponding energies $e_\alpha^{(1)}$.

4) One repeats steps 2) and 3) until the difference between $|\alpha^{(n-1)}\rangle$ and $|\alpha^{(n)}\rangle$ is small enough

Koopmans theorem

Assuming that single-particle wave functions $\{\psi_\alpha\}_{\alpha=1,\infty}$ do not change when adding or removing a nucleon, one has

$$E^{HF}\left[\{\psi_\alpha\}_A + \psi_a\right] - E^{HF}\left[\{\psi_\alpha\}_A\right] = +\varepsilon_a$$

$$E^{HF}\left[\{\psi_\alpha\}_A - \psi_i\right] - E^{HF}\left[\{\psi_\alpha\}_A\right] = -\varepsilon_i$$

→ Non-trivial result given that $E^{HF} \neq \sum_{i=1}^{A} \varepsilon_i$

→ Provides $\{\varepsilon_\alpha\}$ with a clear physical meaning (within the HF approximation)

→ Bad approximation of the observable $E_k^{A\pm1} - E_0^A$ if HF is missing important correlations

Beyond HF approximation

Going back to the normal-ordered form of the Hamiltonian

$$H = \underbrace{E^{HF} + \sum_{\alpha\beta} h_{\alpha\beta} :a_\alpha^\dagger a_\beta:}_{=H_0} + \underbrace{\frac{1}{4}\sum_{\alpha\beta\gamma\delta} \bar{v}_{\alpha\beta\gamma\delta} :a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma:}_{=H_1}$$

HF approximation = neglect H_1 and work only with $H^{HF} = H_0$

In the HF basis

$$H^{HF} = E^{HF} + \sum_\alpha \varepsilon_\alpha :a^\dagger_\alpha a_\alpha:$$

$$\Rightarrow H^{HF}|\Phi\rangle = E^{HF}|\Phi\rangle$$

but, also, H^{HF} displays other eigenstates that can be depicted as particle-hole (ph) excitations on top of the reference vacuum

$$H^{HF}|\Phi^{abc\ldots}_{ijk\ldots}\rangle = E^{abc\ldots}_{ijk\ldots}|\Phi^{abc\ldots}_{ijk\ldots}\rangle$$

where

$$|\Phi^{abc\ldots}_{ijk\ldots}\rangle \equiv a^\dagger_a a^\dagger_b a^\dagger_c \ldots a_k a_j a_i :|\Phi\rangle$$

$$E^{abc\ldots}_{ijk\ldots} \equiv E^{HF} + \varepsilon_a + \varepsilon_b + \varepsilon_c \ldots - \varepsilon_i - \varepsilon_j - \varepsilon_k - \ldots$$

The set of these eigenstates form a complete basis of the A-body Hilbert space.

The exact ground-state energy is

$$E_0 = E^{HF} + \Delta E_0^{HF}$$

(due to effects of H_1)

→ Various methods (many-body techniques) exist to compute ΔE_0^{HF} (MBPT, CC, NCSM, ...)

- MBPT: many-body perturbation theory
- CC: coupled cluster
- NCSM: no-core shell model