

B.2 Many-electron atoms

- Direct & exchange interactions (between electrons)

N -electron state (Fock representation)

$$|\varphi^N\rangle = |n_1, n_2, \dots, n_e, \dots\rangle$$

n_e : no. of particles in single-particle state $|e\rangle$

- occupation number operator :

$$N = a_e^\dagger a_e$$

$$\text{with } a_\mu^\dagger a_\nu^\dagger + a_\nu^\dagger a_\mu^\dagger = 0$$

$$a_\mu a_\nu + a_\nu a_\mu = 0$$

$$a_\mu a_\nu^\dagger + a_\nu^\dagger a_\mu = \delta_{\mu\nu}$$

Fermi-Dirac statistics

$$\rightarrow a_\mu^\dagger a_\mu^\dagger = 0 \quad (\text{Pauli exclusion principle})$$

$$N_e |\varphi^N\rangle = n_e |\varphi^N\rangle$$

a_e^\dagger, a_e : create/destroy one particle in $|e\rangle$

Hartree-Fock method

Describe system of interacting fermions as an effective single-particle problem, introducing a mean-field single-particle potential $v^{\text{HF}}(\vec{r})$.

$v^{\text{HF}}(\vec{r}) \hat{=} \text{averaged effect of } (N-1) \text{ particles \& (time-dependent) external fields on any given electron.}$

- Exact Hamiltonian (coordinate representation, pair interactions only)

$$H_N = \sum_{i=1}^N \left\{ \underbrace{-\frac{\hbar^2}{2m} \Delta_i + V(\vec{r}_i)}_{h_i} \right\} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N V(\vec{r}_i, \vec{r}_j)$$

can include time-dep. external fields

- approx. Hamiltonian

$$H_N^{HF} = \sum_{i=1}^N \underbrace{\left(\frac{\hbar^2}{2m} \Delta_i + V^{HF}(\vec{r}_i) \right)}_{h_i^{HF}}$$

HF potential, to be constructed

$$H_N^{HF} \phi_N = E_N \phi_N, \quad \phi_N(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \det(\psi_i(\vec{r}_j))$$

↑ orbitals

$$\hbar^2 \psi_i = \tilde{\epsilon}_i \psi_i, \quad \sum_{j=1}^e m_e = N$$

"Slater determinant for anti-symmetrization"

$$\phi_N(\vec{r}_1, \dots, \vec{r}_N) = \sqrt{N!} \langle \vec{r}_1, \dots, \vec{r}_N | (a_e^\dagger)^{m_e} \dots (a_1^\dagger)^{m_1} | 0 \rangle$$

- Ritz' variational method

Determine ϕ_N with minimal E_N by variation: $\psi_\alpha \rightarrow \psi_\alpha + \delta \psi_\alpha$

$$\frac{\partial}{\partial \psi_\alpha} \left\{ \langle \phi_N | H_N | \phi_N \rangle - \sum_{i=1}^N \epsilon_i \int d\vec{r}' |\psi_i(\vec{r}')|^2 \right\} \stackrel{!}{=} 0$$

↑ variational derivative

↑ Lagrange parameters to guarantee $\|\psi_i\| = 1$

⇒ HF equations

$$\left\{ -\frac{\hbar^2}{2m} \Delta + V(\vec{r}) + \underbrace{\int d\vec{r}' g(\vec{r}') V(\vec{r}, \vec{r}')}_{\text{local}} \right\} \psi_\alpha(\vec{r}) - \underbrace{\int d\vec{r}' g(\vec{r}, \vec{r}') V(\vec{r}, \vec{r}') \psi_\alpha(\vec{r}')}_{\text{non local, due to exchange}} = \epsilon_\alpha \psi_\alpha(\vec{r})$$

$$g(\vec{r}) := \sum_{\substack{i=1 \\ \text{occ}}}^N \psi_i^*(\vec{r}) \psi_i(\vec{r})$$

$$S(F, F') := \sum_{\substack{i=1 \\ \text{occ}}}^N \langle \varphi_i^*(F') | \varphi_i(F) \rangle$$

$$\Leftrightarrow \left\{ -\frac{\hbar^2}{2m} \Delta + V^{\text{HF}} \right\} \varphi_\alpha = E_\alpha \varphi_\alpha, \quad E_\alpha \in \mathbb{R}$$

- Self consistent solution of HF equations

Step 0 : approximate (start) orbitals : $\{ \varphi_i^{(0)} \}_{i=1 \dots N}$

calculate $V^{\text{HF}(0)} [\{ \varphi_i^{(0)} \}]$

Step 1 : solve eigenvalue problem

$$\left(\pm + V^{\text{HF}(0)} \right) \varphi_\alpha^{(1)} = E_\alpha^{(1)} \varphi_\alpha^{(1)}$$

\Rightarrow ∞ many solutions (in general)

Select $\{ \varphi_1^{(1)}, \dots, \varphi_N^{(1)} \}$ corresponding to N lowest energies $E_\alpha^{(1)}$, $\alpha=1 \dots N$ (no degeneracy assumed).

Only these orbitals are occupied in the N particle ground state.

Step n : solve eigenvalue problem

$$\left(\pm + V^{\text{HF}(n-1)} \right) \varphi_\alpha^{(n)} = E_\alpha^{(n)} \varphi_\alpha^{(n)}$$

$n \rightarrow \infty$ (convergence assumed)

self consistent orbitals & orbital energies

$$\varphi_\alpha = \lim_{n \rightarrow \infty} \varphi_\alpha^{(n)}$$

$$E_\alpha = \lim_{n \rightarrow \infty} E_\alpha^{(n)}$$

From $\{ |e_\alpha\rangle \} =: \{ |\alpha\rangle \}$ build self consistent
 N electron ground state ϕ_N^{HF} with energy

$$\begin{aligned}
 E_N^{\text{HF}} &= \langle \phi_N^{\text{HF}} | \hat{H}_N | \phi_N^{\text{HF}} \rangle \\
 &= \sum_{i=1}^N \langle i | h | i \rangle + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \{ \langle i,j | V | i,j \rangle - \langle i,j | V | j,i \rangle \} \\
 &\quad \text{direct} \qquad \text{exchange} \\
 &\qquad \qquad \qquad \text{interaction} \\
 &\neq \sum_{\alpha=1}^N \epsilon_\alpha
 \end{aligned}$$

Density functional theory (DFT)

Focus on electron density rather than electronic orbitals as in HF method.

Better for large systems (molecules, clusters, solid), where HF becomes numerically inaccessible.

N electron system (non-relativistic):

$$\hat{H} = \sum_{i=1}^N \left\{ \frac{1}{2} p_i^2 + v(\vec{r}_i) \right\} + \sum_{i < j=1}^N \frac{1}{r_{ij}}, \quad r_{ij} = |\vec{r}_i - \vec{r}_j|$$

Single electron number density

$$\rho(\vec{r}) := \int d\vec{r}_2 \dots d\vec{r}_N \underbrace{|\varphi_N(\vec{r}_1, \dots, \vec{r}_N)|^2}_{\text{exact ground state wf.}}$$

Hohenberg & Kohn: ρ uniquely determines every observable of a stationary many-electron system, e.g., the ground-state energy:

$$E[\rho] = T[\rho] + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d\vec{r} v(\vec{r}) \rho(\vec{r}) + E_{xc}[\rho]$$

electron-nuclei interaction
many-electron exchange-correlation energy

$$T[\rho] = \frac{1}{2} \sum_{i=1}^N \int d\vec{r} |\nabla \varphi_i(\vec{r})|^2$$

where $\rho(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2$

- Minimize $E[\rho]$ as functional of ρ

\Leftrightarrow Kohn-Sham equations

$$\left[\frac{1}{2} \Delta + V_{\text{eff}}(\vec{r}) \right] \varphi_i(\vec{r}) = \epsilon_i \varphi_i(\vec{r})$$

$$V(\vec{r}) + \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \underbrace{\frac{\delta E_{xc}}{\delta \rho}}_{= V_{xc}(\vec{r})}$$

Lagrange multiplier (for $\|\rho\| = 1$)
 exchange-corr. potential

- Important: Finding good approximation for V_{xc}

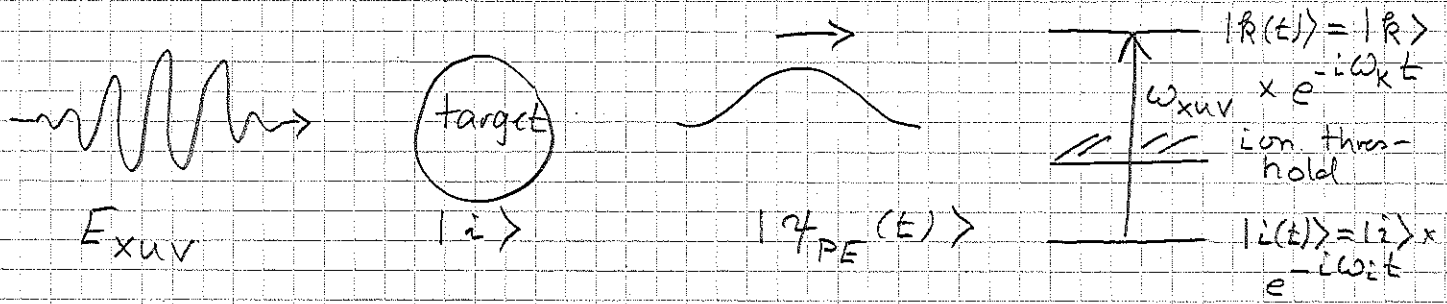
Simplest version: local-density approximation

Relevance: Numerically tractable for large systems, but finding good V_{xc} is difficult.

2. Time-resolved electron emission

C. Streaking spectroscopy

C.1 Photoemission phase shifts and time delays



Basic scenario of photoionization by an electromagnetic pulse from an initial state $|i\rangle$, generating a photoelectron wave packet $|\psi_{PE}(t)\rangle$.

- Initial / final state :

$$H_{tar} |i\rangle = \omega_i |i\rangle ; H_{tar} |R\rangle = \omega_R |R\rangle$$

Neglect all bound target states, except $|i\rangle$:

$$|\psi(t)\rangle = g(t) |i(t)\rangle + \int dR a_R(t) |R(t)\rangle$$

initial conditions: $g(-\infty) = 1 ; a_R(-\infty) = 0$

- Solve TDSE for "weak" external field (single-photon ionization):

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = (H_{tar} + V_{xuv}(t)) |\psi(t)\rangle$$

$$\langle R' | V_{xuv} | R \rangle \approx 0 \quad (\text{no cont.-cont. coupling in "weak" fields})$$

\Rightarrow (1. order TD perturbation theory)

$$g(t) = 1 \quad (\text{no initial-state depletion})$$

$$a_R(t) = -i \int_{-\infty}^t dt' \langle R(t') | V_{xuv}(t') | i(t') \rangle$$

\downarrow lin polarization
 $= z E_{xuv}(t)$ (length form)

For sufficiently long times, the photoelectron wave packet no longer overlaps with the target

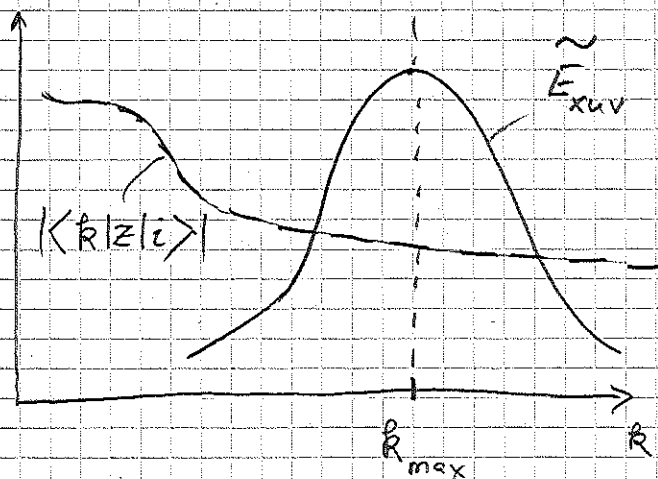
$$\begin{aligned}
|\psi_{PE}(t)\rangle &\approx \int dR a_R(t) |R(t)\rangle \\
&= i \int dR |R\rangle e^{-i\omega_R t} \langle R|Z|z\rangle \int dt' \\
&\quad \times \underbrace{(2\pi)^{-1/2} \int d\omega \tilde{E}_{XUV}(\omega) e^{-i\omega t'}}_{= E_{XUV}(t')} e^{\underbrace{i(\omega_R - \omega) t'}_{= \omega_R t}} \\
&\sim \sqrt{2\pi} i \int dR |R\rangle \langle R|Z|z\rangle \tilde{E}_{XUV}(\omega_{Ri}) e^{-i\omega_R t}
\end{aligned}$$

- o the (XUV) pulse spectral profile gets imprinted on the photoelectron wave packet
- o photon electron dispersion ω_R matters (for free electron only: $\omega_R = \frac{1}{2} R^2$)

Assume:

- $\tilde{E}_{XUV}(\omega_{Ri})$ centered at R_{max}

- $\langle R|Z|z\rangle$ monotonously decreasing (for "large" R)



- o dominant spectral component of $|\psi_{PE}\rangle$ slightly red-shifted from R_{max} .

In position representation:

$$\psi_{PE}(z, t) = \langle z | \psi_{PE}(t) \rangle$$

$$\sim \int dR |\langle R|z|z\rangle| \tilde{E}_{xuv}(\omega_{Ri}) e^{i \arg \langle R|z|z\rangle} \\ \times \underbrace{\langle z|R\rangle}_{\sim e^{iRz}} e^{-i\omega_R t}$$

Taylor expand dipole phase about R_{max} :

$$\arg \langle R|z|z\rangle = \arg \langle R_{max}|z|z\rangle + \underbrace{\left. \frac{d}{dR} \arg \langle R|z|z\rangle \right|_{R_{max}}}_{=: \bar{z}} (R - R_{max}) + \dots$$

$$\Rightarrow |\psi_{PE}(z,t)|^2 \sim \left| \int dR |\langle R|z|z\rangle| \tilde{E}_{xuv}(\omega_{Ri}) \times e^{iR(z - \bar{z}) - i\omega_R t} \right|^2$$

- Interpretation:

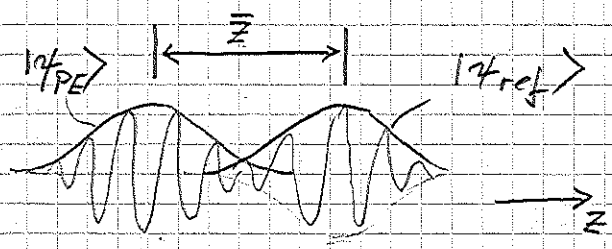
\bar{z} : PE wavepacket displacement from hypothetical reference wave packet with $\bar{z}_{ref} = 0$

$\bar{t} = \bar{z} / v_g$: time needed to catch up with reference wavepacket

$v_g = \left. \frac{d\omega_R}{dR} \right|_{R_{max}}$: group velocity

For $\omega_R = \frac{R^2}{2}$:

$$v_g = R_{max}$$



$$\bar{t} = - \left. \frac{d}{d\omega} \arg \langle R|z|z\rangle \right|_{R_{max}}$$

$$\langle z \rangle = \lim_{\text{large } t} \langle z \rangle_{ref} - \bar{z}$$

$$\downarrow \\ \langle \psi_{PE}(t) | z | \psi_{PE}(t) \rangle$$

\bar{t} as delayed start time relative to reference wavepacket

