

Hamiltonian for the entire problem

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Kinetic energy of all ~~the~~ particles in the solid

+

Their interaction energies

Solid — two groups of electrons.

Valence electrons
which contribute to
chemical bonding

core electrons

tightly bound in the closed shells
of the lattice ions (hardly influence
the properties of the solid)

Consequently — consider the valence electrons and the
lattice ions as independent constituents of the
solid

It is not always that one can make such a clear
distinction.

Hamiltonian

$$H = H_{el} + H_{ion} + H_{el-ion} + H_{ex}, \quad \text{--- (1)}$$

H_{ex} = energy associated with interactions with external fields
For the time being neglect it.

For the electron part

$$\begin{aligned}
 H_{\text{el}} &= H_{\text{el,kin}} + H_{\text{el-el}} \\
 &= \sum_k \frac{\vec{p}_k^2}{2m} + \underbrace{\frac{1}{8\pi\epsilon_0} \sum'_{k,k'} \frac{e^2}{|\vec{r}_k - \vec{r}_{k'}|}}_{\text{Coulomb term for the interaction}} \quad \text{--- (2)}
 \end{aligned}$$

\sum' → exclude $k=k'$.

\vec{p}_k , \vec{r}_k , and m are the momentum, position, and mass of an electron of index k .

For the ion part

$$\begin{aligned}
 H_{\text{ion}} &= H_{\text{ion,kin}} + H_{\text{ion-ion}} \\
 &= \sum_i \frac{\vec{p}_i^2}{2M_i} + \frac{1}{2} \sum'_{ii'} V_{\text{ion}} (\vec{R}_i - \vec{R}_{i'}) \quad \text{--- (3)}
 \end{aligned}$$

- Left open the explicit form of the ion-ion interaction,
- Assumed that it can be described as a sum over two-particle interactions, each dependent only on the difference in the ion coordinates \vec{R}_i .

For the electron-ion interaction

$$H_{\text{el-ion}} = \sum_{k,i} V_{\text{el-ion}} (\vec{r}_k - \vec{R}_i), \quad \text{--- (4)}$$

Periodic arrangement of the ions in the lattice

It is equilibrium positions, about which the ions vibrate, which shows strong periodicity, rather than their actual positions at any instant.

Therefore, divide the ion-ion interaction into two components, one describing the interaction when the ions are in their equilibrium position, the other, a correction to account for the vibrations of the lattice

$$H_{\text{ion-ion}} = H_{\text{ion-ion}}^0 + H_{\text{ph}}, \quad \text{--- (5)}$$

$$H_{\text{el-ion}} = H_{\text{el-ion}}^0 + H_{\text{el-ph}}, \quad \text{--- (6)}$$

The index ph for the lattice vibration term describes refers to the phonons.

Equations (1)–(6) provide the foundation for the quantum mechanical treatment of most solid-state properties.

Next step → transition from the Hamiltonian function to the Hamiltonian operator.

Coordinate representation — the Hamiltonian operator depends on all the coordinates of all electrons and ions. Thus correspondingly, the wavefunction on which the Hamiltonian operates becomes a function of all these coordinates.

⇒ Note

that this form of the Hamiltonian allows only limited account to be taken of the electron spin.

However for most of the problems that we will be concerned with the non-relativistic Schrödinger equation without spin-orbit coupling terms will suffice.

⇒ Note that in general it is not possible to solve rigorously the above quantum mechanical properties.

There are two ways in which the problem in general can be simplified.

The individual terms of the Hamiltonian may be neglected or partially considered, or treated subsequently as perturbations.

The problem thus simplified is then further simplified using the symmetry of the lattice.

Note these approximations are contextual and depend on the questions that we are trying to answer and on the nature of the solid.

There is a problem in completely neglecting individual terms of the Hamiltonian, since all interactions - being always Coulombic - are equally strong.

Consider the electronic part of the full Hamiltonian

$$H_{\text{el}} = H_{\text{el,kin}} + H_{\text{el-el}}.$$

This cannot be considered alone!

What does this describe? It describes an electron gas whose charge is not compensated by ions in the solid.

How to proceed?

We can extend the above Hamiltonian to include a uniform (constant) space charge δ_+ :

- (i) this would represent the average charge of the ions;
- (ii) will take care of the interaction of the electrons with this space charge.

Let these two terms ~~be~~ together be represented by H_+ , then we can write the Hamiltonian for this approximation as

$$H_{\text{el}} = - \sum_{\mathbf{k}} \frac{\hbar^2}{2m} \nabla_{\mathbf{k}}^2 + \frac{1}{8\pi\epsilon_0} \sum_{\mathbf{k}\mathbf{k}'}' \frac{e^2}{|\delta_{\mathbf{k}} - \delta_{\mathbf{k}'}|} + H_+ . \quad \rightarrow (7)$$

The electron gas is embedded in a constant positive background. This model is often called as the "jellium" model.

⇒ This completely suppresses the lattice symmetry aspects while brings the electron gas aspects, particularly the electron-electron interactions, to the fore.

\rightarrow Many properties of the

Many of the properties of metals can be described by means of this approximation.

Movement of the ions

Starting with $H_{\text{ion}} = H_{\text{ion,kin}} + H_{\text{ion-ion}}$ and

$H_{\text{ion-ion}} = H_{\text{ion-ion}}^0 + H_{\text{ph}}$, we can arrive at a similar equation for describing the movement of the ions.

Here we introduce a constant negative space charge s_- to take account of the neglected electrons and a term to represent their interaction with the ions.

Let us put these two additions into a single term H_- , we have

$$H_{\text{ion}} = - \sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + \frac{1}{2} \sum_{ii'}' V_{\text{ion}}(\vec{R}_i - \vec{R}_{i'}) + H_- \quad \text{--- (8)}$$

This Hamiltonian forms the basis for the study of lattice dynamics.

The two terms H_+ and H_- exactly cancel each other.

Go back to the equation ①, now we are left with only $H_{\text{el-ion}}$ the term which couples electron and ion motion. Note that we have neglected the H_{ex} term for the time being.

We can separate the interaction of the electrons with the "static" lattice H_{lattice} from $H_{\text{el-ion}}$ and add this component to H_{el} , then the only remaining coupling between electrons and ions is the electron-phonon interaction $H_{\text{el-ph}}$.

This coupling can be dealt with in most cases by perturbation theory.

What did we achieve?

We have divided the initial solid state problem into two components.

- (1) The movement of the electrons in a stationary lattice;
- (2) The movement of the ions in a uniform space charge of electrons.

Note that this decoupling of the total system requires rigorous justification.

The so-called adiabatic approximation (Born - Oppenheimer method) is often used to provide such justification.

Born- Oppenheimer approximation/Method

This approximation is based on the following argument.

The Electrons and ions have very different masses.

The Ions can respond only slowly to a change in the electrons configuration, while the electrons respond adiabatically to a change in the positions of the ions.

Now as far as the motion of electrons is concerned, it is only the instantaneous configuration of the ions which is of interest.

→ As a first approximation we can therefore adopt for the electrons a Schrödinger equation of the form

$$(H_{el} + H_{el-ion})\psi = E_{el}\psi \quad \text{--- (9)}$$

in which the coordinates of the ions are kept fixed.

⇒ The wavefunction depends only on the coordinates of the electrons,

⇒ The coordinates of the ions appear in the equation as parameters,

⇒ As a starting point for a solution of the total problem we now use the product

$$\Psi = \psi(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_{N'}) \varphi(\vec{R}_1, \dots, \vec{R}_{N'}) \quad \text{--- (10)}$$

where ψ are solutions of eqn (9) and N, N' denote the number of electrons and ions.

Substitute this into the Schrödinger equation with eqn. ① as the Hamiltonian, we have

$$H\Psi = (H_{el} + H_{ion} + H_{el-ion})\Psi \Psi$$

$$= (H_{el} + H_{el-ion})\Psi \Psi + H_{ion}\Psi \Psi$$

$$\Rightarrow H_{ion} \xrightarrow{\text{has}} H_{\text{Lankin}} = -\sum_i \frac{k^2}{2M_i} \nabla_i^2$$

$$-\sum_i \frac{k^2}{2M_i} \nabla_i^2 (\Psi \Psi) = -\frac{k^2}{2M_i} \nabla_i (\Psi \nabla_i \Psi + \nabla_i \Psi \cdot \nabla_i \Psi)$$

$$= -\frac{k^2}{2M_i} \left(\Psi \nabla_i^2 \Psi + \nabla_i \Psi \cdot \nabla_i \Psi + \nabla_i \Psi \cdot \nabla_i \Psi + \underline{\Psi \nabla_i^2 \Psi} \right)$$

$$\Rightarrow H\Psi = \Psi (H_{ion} + E_{el})\Psi - \sum_i \frac{k^2}{2M_i} (\Psi \nabla_i^2 \Psi + 2\nabla_i \Psi \cdot \nabla_i \Psi)$$

— ⑩

Now if the last term were absent, eqn. ⑩ $\Psi = \Psi \Psi$ would be separation ansatz which would effectively decouples electron and ion motion.

Thus, for the movement of the ions an eqn. of the form

$$(H_{ion} + E_{el})\Psi = E\Psi$$

— ⑪

would follow.

Note that E_{el} still depends on the ion positions and therefore provides a contribution from the electrons to the potential energy of the ions.

- Note that Eqn. (12) is a Schrödinger equation which involves only the coordinates of the ions. It therefore describes the motion of the ions.
- To describe the motion of the electrons, we replace in eqn. (9) the instantaneous positions of the ions by their mean positions, i.e., we replace Helium by H^0 -ion.
- The last term in eqn. (11) couples the electron and ion systems.
 One can show that it provides only a small contribution to the total energy of the system in the state Ψ .
 However, this is not a proof that this term only describes a weak interaction which can subsequently be treated by perturbation theory.
- The justification for the ansatz eqn. (10) is also doubtful. The Schrödinger eqn. (9) has as its solution not one eigenfunction ψ but a complete set of eigenfunctions ψ_m . The ansatz (10) should therefore be written as an expansion in terms of this set of eigenfunctions. The restriction to a single wave function neglects all electron transitions induced by the ion motion.
- This basis approximation has problems and calls for a more exact analysis. We will not take it up here.

SUMMARY

For the electrons.

$$\boxed{(\text{H}_{\text{el}} + \text{H}_{\text{ion}})\psi = E_{\text{el}}\psi} \longrightarrow \textcircled{1}$$

For the total system

$$\psi = \psi_e \psi_i \longrightarrow \textcircled{2}$$

we did something, and got

$$H\psi = \psi (\text{H}_{\text{ion}} + E_{\text{el}})\psi - \sum_k \frac{\hbar^2}{2m} \underbrace{(\psi \nabla_i^2 \psi + 2 \nabla_i \psi \cdot \nabla_i \psi)}_{\text{if. Negligible}} \longrightarrow \textcircled{3}$$

$$E\psi\psi = \psi (\text{H}_{\text{ion}} + E_{\text{el}})\psi$$

$$\Rightarrow \psi [(\text{H}_{\text{ion}} + E_{\text{el}}) - E]\psi = 0$$

$$\psi \neq 0 \Rightarrow \boxed{(\text{H}_{\text{ion}} + E_{\text{el}})\psi = E\psi} \quad \begin{array}{l} \text{depends only} \\ \text{on the ion} \\ \text{coordinates.} \end{array} \quad \textcircled{4}$$

E_{el} still depends on the ion positions. \Rightarrow provides contribution from the electrons to the potential energy of the ions.

Shortcoming of the ansatz $\psi = \psi_e \psi_i$.

Eqn. ① has ~~one~~ its solution not one eigenfunction ψ but a complete set of eigenfunctions ψ_n .

So the ansatz ② should be written in terms as ~~as~~ an expansion in terms of this set of eigenfunctions. The restriction to a single wave function neglects ~~the~~ all electron transitions induced by the ion motion.

The Hartree-Fock Approximation

Let us now focus on the motion of electrons, as described by eqn. ⑦.

Consider an electron gas embedded in a homogeneous, positively charged medium — jellium model — or in a rigid lattice of positively charged ions.

What is the difficulty in tackling the above problem?

Difficulty: the interaction between the individual electrons.

It is a many-body problem.

Now if these interactions were absent, the many-body problem would decouple into one-body problems which describe the movement of an electron in a given potential field.

So it is tempting to ask whether the above many-body problem could be reduced to a one-body problem while including at least parts of the electron-electron interactions.

Answer: Such a reduction is achieved by the Hartree-Fock approximation.

Consider the Hamiltonian

$$H = - \sum_{\mathbf{k}} \frac{\hbar^2}{2m} \nabla_{\mathbf{k}} + \sum_{\mathbf{k}} V(\mathbf{r}_k) + \frac{1}{8\pi G} \sum'_{\mathbf{k}\mathbf{k}'} \frac{e^2}{|\mathbf{r}_k - \mathbf{r}_{k'}|}$$

$$= \sum_{\mathbf{k}} H_k + \sum'_{\mathbf{k}\mathbf{k}'} H_{kk'}, \quad \text{--- (13)}$$

Note that

$$H_{\text{el-ion}}^0 = \sum_{\mathbf{k}} V(\mathbf{r}_k) \text{ and } V(\mathbf{r}_k) = \sum_i V(\mathbf{r}_k - \mathbf{R}_i)$$

Notice that the first two terms in eqn (13) are sums over single-particle operators.

So the solution would be easily obtained, if the relatively strong electron-electron interactions are neglected.

The Schrödinger eqn $\sum_{\mathbf{k}} H_k \Phi = E \Phi$ could be separated by using

$$\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \varphi_1(\mathbf{r}_1) \varphi_2(\mathbf{r}_2) \dots \varphi_N(\mathbf{r}_N), \quad \text{--- (14)}$$

With $E = \sum_k E_k$, it reduces to one-electron equations

$$H_k \varphi_k(\mathbf{r}_k) = E_k \varphi_k(\mathbf{r}_k).$$

⇒ However, the term $H_{kk'}$ in eqn (13) prevents this possibility, as it depends on the coordinates of two particles.

⇒ Inspite of the above difficulty, the ansatz (14) allows us to derive an approximate solution which contains parts of the electron-electron interaction.

→ Insert this ansatz function in the Schrödinger equation $H\Phi = E\Phi$ with H given by eqn. (13).

→ Calculate the expectation value of the energy

$$E = \langle \Phi | H | \Phi \rangle.$$

Note that

→ $H \rightarrow$ sum of single-particle operators H_k and two-particle operators $H_{kk'}$, the matrix elements become products of integrals $\langle \varphi_n | H_k | \varphi_k \rangle$ or $\langle \varphi_n \varphi_{k'} | H_{kk'} | \varphi_n \varphi_{k'} \rangle$ and integrals $\langle \varphi_j | \varphi_j \rangle$ ($j \neq k, k'$),

Assume that the φ_k are normalized to unity.

$$\rightarrow E = \langle \Phi | H | \Phi \rangle$$

$$= \sum_k \langle \varphi_k | H_k | \varphi_k \rangle + \frac{e^2}{8\pi G_0} \sum'_{kk'} \left\langle \varphi_k \varphi_{k'} \left| \frac{1}{|\mathbf{r}_k - \mathbf{r}_{k'}|} \right| \varphi_k \varphi_{k'} \right\rangle,$$

— (15)

This is only the expectation value of the energy for arbitrarily given φ_k .

→ Use variational principle to obtain those φ_k that minimize E to represent the best set of functions for the ground state, of course within the limits of the ansatz.

→ Vary eqn. (15) for any ψ_k^* or ψ_k and equate the variation to zero. Also add the normalization conditions (multiplied with Lagrange parameters β_k) to eqn. (15) and carry out the variation

$$\delta \left(E - \sum_k (\langle \psi_k | \psi_k \rangle - 1) \right) = 0,$$

→ This yields

$$\begin{aligned} & \langle \delta \psi_j | H_j | \psi_j \rangle + \frac{e^2}{4\pi\epsilon_0} \sum_{k(\neq j)} \langle \delta \psi_j | \psi_k \rangle \frac{1}{|\vec{r}_k - \vec{r}_j|} \langle \psi_j | \psi_k \rangle - E_j \langle \delta \psi_j | \psi_j \rangle \\ &= \langle \delta \psi_j | H_j + \frac{e^2}{4\pi\epsilon_0} \sum_{k(\neq j)} \langle \psi_k | \frac{1}{|\vec{r}_k - \vec{r}_j|} | \psi_k \rangle - E_j | \psi_j \rangle = 0. \end{aligned} \quad \rightarrow (17)$$

This equation must remain valid regardless of the variation $\delta \psi_j^*$, it follows that the ψ_j are defined by the equation

$$\boxed{\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \sum_{k(\neq j)} \int \frac{|\psi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \right] \psi_j(\vec{r}) = E_j \psi_j(\vec{r})} \quad \rightarrow (18)$$

The positions of the j th and the k th electrons are represented by \vec{r} and \vec{r}' , respectively.

⇒ Note that eqn. (18) is a single-particle Schrödinger equation, the "Hartree equation".

The Hartree equation describes an electron (j) at location \vec{r} in the potential field $V(\vec{r})$ of the lattice ions, and in the Coulomb potential of an average distribution of all other electrons ($k \neq j$).

The Lagrange parameters E_k have the meaning of one-electron energies.

Consider

$$\Phi(\vec{r}_1 \dots \vec{r}_N) = \varphi_1(\vec{r}_1) \varphi_2(\vec{r}_2) \dots \varphi_N(\vec{r}_N).$$

Apply the Pauli principle and extend the above wave function to construct an anti-symmetric wavefunction.

Written in the form of a wave determinant the wave function reads

$$\Phi = (N!)^{-\frac{1}{2}} \begin{vmatrix} \varphi_1(\vec{q}_1) & \dots & \varphi_N(\vec{q}_1) \\ \varphi_1(\vec{q}_2) & \dots & \varphi_N(\vec{q}_2) \\ \vdots & & \vdots \\ \varphi_1(\vec{q}_N) & \dots & \varphi_N(\vec{q}_N) \end{vmatrix}, \quad (19)(a)$$

where the factor in front of the determinant ensures normalization.

$\left\{ \begin{array}{l} \varphi_j \rightarrow \text{orthogonal} \\ \varphi_j(\vec{q}_n) \rightarrow \text{wavefunction for the } j^{\text{th}} \text{ electron with} \\ \text{coordinates } \vec{q}_k \text{ (spatial coordinates } \vec{r}_k \text{,} \\ \text{and spin coordinate).} \end{array} \right.$

→ If two electrons are interchanged, two columns of the determinant are interchanged and Φ changes sign.

→ If two electrons have the same coordinates, two columns are identical and Φ vanishes.

$$\rightarrow \Phi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \varphi_{P_1}(\vec{q}_1) \varphi_{P_2}(\vec{q}_2) \dots \varphi_{P_N}(\vec{q}_N),$$

→ (19)(b)

→ Compute the expectation value $E = \langle \Phi | H | \Phi \rangle$.

$$H = - \sum_k \underbrace{\frac{\hbar^2}{2m} \nabla_k^2}_{H_k} + \sum_k V(\vec{r}_k) + \underbrace{\frac{1}{8\pi\epsilon_0} \sum'_{kk'} \frac{e^2}{|\vec{r}_k - \vec{r}_{k'}|}}_{H_{kk'}}$$

$$= \sum_k H_k + \sum_{kk'} H_{kk'}$$

$$E = \sum_k \int \varphi_k^*(\vec{q}_1) H_k \varphi_k(\vec{q}_1) d\vec{q}_1 + \frac{e^2}{8\pi\epsilon_0} \sum'_{kk'} \int \frac{|\varphi_k(\vec{q}_1)|^2 |\varphi_{k'}(\vec{q}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{q}_1 d\vec{q}_2$$

$$\boxed{- \frac{e^2}{8\pi\epsilon_0} \sum'_{kk'} \int \frac{\varphi_k^*(\vec{q}_1) \varphi_k(\vec{q}_2) \varphi_{k'}^*(\vec{q}_2) \varphi_{k'}(\vec{q}_1)}{|\vec{r}_1 - \vec{r}_2|} d\vec{q}_1 d\vec{q}_2.}$$

(The integration here includes a summation over the spin variables.) (20)

→ an extra term has appeared.

The modified variational equation is

$$\delta \left[E - \sum_{kk'} \gamma_{kk'} (\langle \varphi_k | \varphi_{k'} \rangle - \delta_{kk'}) \right] = 0, \quad \text{--- (21)}$$

where we have taken account of the additional condition of orthogonality.

Carrying out the variation we obtain

$$\left[-\frac{\hbar^2}{2m} \nabla_1^2 + V(\vec{r}_1) \right] \varphi_k(\vec{q}) + \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k' \\ (\neq k)}} \int \frac{|\varphi_{k'}(\vec{q}_2)|^2}{|\vec{r}_1 - \vec{r}_2|} d\tau_2 \varphi_{k'}(\vec{q}) - \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k' \\ (\neq k)}} \int \frac{\varphi_{k'}^*(\vec{q}_2) \varphi_{k'}(\vec{q}_2)}{|\vec{r}_1 - \vec{r}_2|} d\tau_2 \varphi_{k'}(\vec{q}) = \sum_{k'} \lambda_{kk'} \varphi_{k'}(\vec{q}) \quad (22)$$

→ matrix $\lambda_{kk'}$ can be diagonalized by introducing a transformation

$$\varphi'_i = \sum_k U_{ik} \varphi_k,$$

where U_{ik} is an appropriately chosen unitary matrix.

$$\lambda'_{kk'} = E_k \delta_{kk'}$$

→ Now relabel φ' as φ , so the LHS remains unchanged, whereas the RHS becomes $E_k \varphi_k(\vec{q})$.

→ In the absence of spin-orbit coupling, every wave function can be written as the product of a space function and a spin function.

→ Last term on LHS: Just a summation over electrons with the same spin, because the orthogonality of the spin functions causes the other spin terms to disappear. So spin does not appear explicitly any further.

Finally we have

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi_j(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \sum_{k \neq j} \int \frac{|\varphi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \varphi_j(\vec{r}') \\ - \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{k \neq j \\ \text{Spin } \uparrow \downarrow}} \int \frac{\varphi_k^*(\vec{r}') \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \varphi_k(\vec{r}) = E_j \varphi_j(\vec{r}).$$

— (23)

This is the Hartree-Fock equation.

Meaning of the quantities E_k , which were introduced as Lagrange parameters.

To answer the above question let us try to ask the following question, what is the change of energy of the electron system when one of the N electrons (e.g., the i th) is removed from it?

→ Assume that in view of the large number of electrons in the system, the removal of the i th electron will not alter the other Ψ_k ($k \neq i$).

The change of energy is

$$\Delta E = \langle \tilde{\Phi}' | H | \tilde{\Phi}' \rangle - \langle \tilde{\Phi} | H | \tilde{\Phi} \rangle, \quad \text{--- (24)}$$

where $\tilde{\Phi}'$ is obtained from $\tilde{\Phi}$ by removing the i th row and column in the determinant giving $\tilde{\Phi}$.

Recall the expression for $E = \langle \tilde{\Phi} | H | \tilde{\Phi} \rangle$, now if the above subtraction is carried out, the only terms which remain are those in which k or k' is equal to i .

$$\begin{aligned} \Rightarrow -\Delta E &= \int \Psi_i^*(\vec{q}_1) H_{ik} \Psi_i(\vec{q}_1) d\vec{q}_1 + \frac{e^2}{8\pi\epsilon_0} \sum_{k \neq i} \int \frac{|\Psi_k(\vec{q}_1)|^2 |\Psi_k(\vec{q}_2)|^2}{|\vec{q}_1 - \vec{q}_2|} d\vec{q}_1 d\vec{q}_2 \\ &\quad - \frac{e^2}{8\pi\epsilon_0} \sum_{k \neq i} \int \frac{\Psi_i^*(\vec{q}_1) \Psi_k(\vec{q}_1) \Psi_k^*(\vec{q}_2) \Psi_k(\vec{q}_2)}{|\vec{q}_1 - \vec{q}_2|} d\vec{q}_1 d\vec{q}_2 \\ &= E_i \end{aligned} \quad \text{--- (25)}$$

→ Equal to E_i can be seen by multiplying the Hartree-Fock equation with Ψ_i^* .

So E_i has the meaning of the energy parameter in a one-electron Schrödinger equation.

$-E_i$ is the energy required to remove an electron from the system.

⇒ Or, the energy needed to transfer an electron from state i to state k is $E_k - E_i$.

Koopmans theorem.

Recall the Hartree eqn.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \sum_{k \neq j} \int \frac{|\varphi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \right] \varphi_j(\vec{r}) = E_j \varphi_j(\vec{r}).$$

Rewrite the integral in the third term as follows

$$\sum_{k \neq j} \int \frac{|\varphi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' = \sum_k \int \frac{|\varphi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' - \int \frac{|\varphi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (26)$$

\Rightarrow subtract from the interaction of the observed electron with all electrons (including itself) that part which represents the interaction of the electron with its own space-charge cloud

$$- \frac{e}{4\pi\epsilon_0} \int \frac{\rho_j^H(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \varphi_j(\vec{r}), \quad \rho_j^H(\vec{r}) = -e |\varphi_j(\vec{r})|^2 \quad (27)$$

ρ_j^H just represents one-electron charge, as

$$\int \rho_j^H d\vec{r} = -e.$$

Recall the Hartree-Fock eqn.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi_j(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \sum_{k \neq j} \int \frac{|\varphi_k(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \varphi_k(\vec{r}) - \frac{p_j^2}{4\pi\epsilon_0} \sum_{\substack{k \neq j \\ \text{spins}}} \int \frac{\varphi_k^*(\vec{r}') \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \varphi_k(\vec{r}) = E_j \varphi_j(\vec{r})$$

Now if $k=j$ terms are included in both the sums these additions cancel themselves.

Therefore, the last term on the LHS of the HF eqn. then corresponds to the final term on the RHS of (26). Correspondingly we can write

$$\frac{e^2}{4\pi\epsilon_0} \sum_k_{\text{spin}\parallel} \int \frac{\varphi_k^*(\vec{r}') \varphi_j(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' \varphi_k(\vec{r}) = - \frac{e}{4\pi\epsilon_0} \int \frac{\varphi_j^H(\vec{r}, \vec{r}') d\vec{r}'}{|\vec{r}-\vec{r}'|} \varphi_j(\vec{r}) \quad (28)$$

where

$$\varphi_j^H = -e \sum_k_{\text{spin}\parallel} \frac{\varphi_k^*(\vec{r}') \varphi_j(\vec{r}') \varphi_j^*(\vec{r}) \varphi_k(\vec{r})}{\varphi_j^*(\vec{r}) \varphi_j(\vec{r})}. \quad (29)$$

Thus, in place of the charge density ϱ^H (27), we have the exchange charge density ϱ^H .

[Note that this also represents a charge $-e$, this is apparent by performing an integration over \vec{r}' .]

From (27) and (28) and using the abbreviation $\varrho = \sum_k \varrho_k^H$, the HF equation becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) - \frac{e}{4\pi\epsilon_0} \int \frac{\varrho(\vec{r}') - \varrho_j^H(\vec{r}, \vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' \right] \varphi_j(\vec{r}) = E_j \varphi_j(\vec{r}). \quad (30)$$

The above eqn. is difficult to solve as the interaction term ϱ depends on the φ_j , the solutions we are trying to find.

Therefore, an iterative method is used to solve the equation. We start with a trial function for the ψ_j , evaluate S and then solve the equation to obtain better estimates of the ψ_j .

Next, the new ψ_j are inserted into S and the whole process is repeated until consistent solutions are attained (self-consistent field approximation).

Another difficulty: The interaction term depends on j , so that there is a different Hartree-Fock eqn for each electron.

To help we can use the Slater's approximation which averages the δ_j^{HF} over all j

$$\begin{aligned} \bar{\delta}^{\text{HF}} &= \frac{\sum_j \delta_j^*(\vec{r}) \delta_j(\vec{r}) \delta_j^{\text{HF}}(\vec{r}, \vec{r}')} {\sum_k \delta_k^*(\vec{r}) \delta_k(\vec{r})} = \dots \\ &= -e \frac{\sum_{jk||} \delta_k^*(\vec{r}') \delta_j(\vec{r}') \delta_j^*(\vec{r}) \delta_k(\vec{r})}{\sum_k \delta_k^*(\vec{r}) \delta_k(\vec{r})} \quad \text{--- (31)} \end{aligned}$$

This averaged charge density is then used in eqn (30)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) - \frac{e}{4\pi\epsilon_0} \int \frac{S(\vec{r}') - \bar{\delta}^{\text{HF}}(\vec{r}, \vec{r}')} {|\vec{r} - \vec{r}'|} d\vec{r}' \right] \psi_j(\vec{r}) = E_j \psi_j(\vec{r})$$

--- (32)

Note that the interaction term is now only a fraction of \vec{r} , which we can combine with the second term to represent a local potential field which is equally valid for all electrons.

Thus, we have achieved our goal of splitting up the Schrödinger equation for the many-electron problem into one-electron wave equations.

The Schrödinger eqn for the one-electron approximation contains, through the third term on the LHS, important parts of the electron-electron interaction.