

Solid state

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crystals

nuclear motion

electronic structure

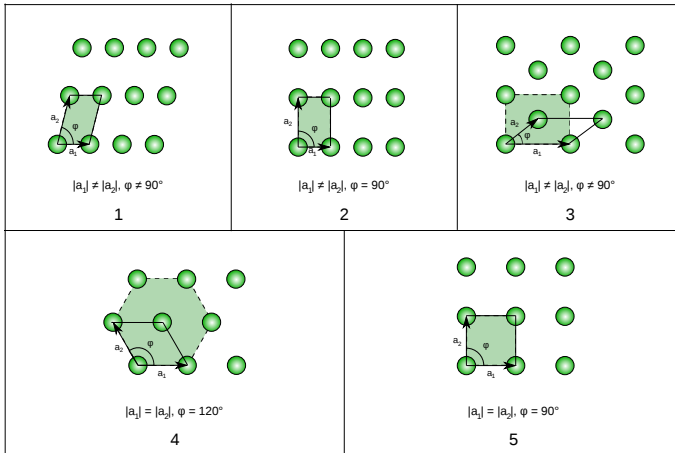


Crystals are model systems characterized by periodicity, i.e. invariance under translation. The 3, 2 and 1-dimensional crystal, therefore, must be invariant under all translation operations:

$$T_{n_1 a_1 + n_2 a_2 + n_3 a_3} \quad T_{n_1 a_1 + n_2 a_2} \quad T_{n_1 a_1}$$

where a_i are 3 independent vectors and n_i are integers. This simple property has many important consequences. Crystals are also often endowed with other (punctual) symmetries, not all of the symmetry operations are however compatible with translational invariance.





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In general we shall expect that for every physical punctual property f of a crystal system we can redefine f with respect to fractional coordinates u :

$$x = u_i a_i, \quad f(x) = \tilde{f}(u) = \tilde{f}(u + n) = f(x + a_i n_i)$$

so that $\tilde{f}(u)$ is periodic in u with period 1 for all u_i . One can fourier expand $\tilde{f}(u)$, e.g. in two dimensions one has:

$$\tilde{f}(u_1, u_2) = \sum_{N_1, N_2} \tilde{F}_{N_1 N_2} e^{2\pi i(N_1 u_1 + N_2 u_2)}$$



However we can also introduce a set of vectors b_i with the same dimensionality of a_i such that:

$$b_i a_j = 2\pi \delta_{ij}.$$

The vectors $k = n_i b_i$ form the “reciprocal lattice” of $x = n_i a_i$, “reciprocal” meaning that it is connected to the fourier transform, which in light of the relation above we may rewrite:

$$f(x) = \sum_{k=b_i n_i} F(k) e^{ikx} \quad (1)$$

$$F(k) = \frac{1}{2\pi} \sum_{x=a_i n_i} f(x) e^{ikx} \quad (2)$$

the sum being on each vector of its lattice.



Quantum eigenfunctions of the hamiltonian must satisfy symmetry requirements in crystal, we are here concerned with the implications of translational symmetry, i.e. the Bloch theorem. According to linear algebra, when two operators do commute with one another, it is always possible to find a set of vectors that are eigenvectors of both operators. Consequently, when one operator is the Hamiltonian and the other one of the translation operators T_x , $x = n_j a_j$:

$$[T_x, H] = 0$$

that is how one expresses the fact that the potential has the periodicity of the crystal, and therefore it must be possible to find the H eigenfunctions $\psi(r)$ so that:

$$\begin{aligned} T_x \psi(r) &= \psi(r - x) = \lambda_x \psi(r) \\ T_{nx} \psi(r) = T_x^n \psi(r) &= \psi(r - nx) = \lambda_x^n \psi(r) \end{aligned}$$

for all integer values of n .



Since λ^n should not grow explosively for either positive or negative n , λ must be of unitary module and we may reword the latter equations:

$$\begin{aligned}T_x \psi_{kj}(r) &= e^{ikx} \psi_{kj}(r) \\ \psi_{kj}(r) &= \phi_{kj}(r) e^{ikr}\end{aligned}$$

that is: all stationary wavefunctions can be classified with a quantum number k in the reciprocal space and each such function can be expressed as a function ϕ with the periodicity of the crystal multiplied by a plane wave e^{ikr} with the same wavevector.



Nuclear motion constitutes an important part of crystal physics, it dictates sound propagation, heat transport, thermodynamic properties and influences charge conduction, molecular adsorption and several other processes.

For brevity, we directly approach the quantum equations of motion, though consideration of the classical solutions provides some insight.



The harmonic oscillator

We shortly review a solution of the quantum harmonic oscillator.

$$H\psi_i = \left(-\frac{p^2}{2m} + \frac{k}{2}x^2\right)\psi_i = \epsilon_i\psi_i$$

The harmonic oscillator really depends on a single parameter, infact:

$$\begin{aligned}\xi &= \sqrt{m}x \\ \eta &= -i\hbar\frac{1}{\sqrt{m}}\frac{d}{dx} = -i\hbar\frac{d}{d\xi} \\ \omega^2 &= \frac{k}{m} \\ H &= \frac{\eta^2}{2} + \frac{\omega^2}{2}\xi^2\end{aligned}$$



We need to introduce 2 new operators:

$$a = \sqrt{\frac{\omega}{2\hbar}} \left(\xi - \frac{1}{i\omega} \eta \right)$$

$$a^\dagger = \sqrt{\frac{\omega}{2\hbar}} \left(\xi + \frac{1}{i\omega} \eta \right)$$

$$\xi = \sqrt{\frac{\hbar}{2\omega}} (a^\dagger + a)$$

$$\eta = i\sqrt{\frac{\hbar\omega}{2}} (a^\dagger - a)$$



We need to introduce 2 new operators and their commutation relations:

$$a = \sqrt{\frac{\omega}{2\hbar}} \left(\xi - \frac{1}{i\omega} \eta \right)$$

$$a^\dagger = \sqrt{\frac{\omega}{2\hbar}} \left(\xi + \frac{1}{i\omega} \eta \right)$$

$$\xi = \sqrt{\frac{\hbar}{2\omega}} (a^\dagger + a)$$

$$\eta = i\sqrt{\frac{\hbar\omega}{2}} (a^\dagger - a)$$

$$[a, a^\dagger] = \frac{\omega}{2\hbar} \left(\frac{1}{i\omega} [\xi, \eta] - \frac{1}{i\omega} [\eta, \xi] \right) = 1$$

$$[a, a] = [a^\dagger, a^\dagger] = 0$$



We are now in position to substitute

$$H = \frac{\hbar\omega}{2}(a^\dagger a + aa^\dagger) = \frac{\hbar\omega}{2}(a^\dagger a + \frac{1}{2}) = \frac{\hbar\omega}{2}(\hat{n} + \frac{1}{2})$$

and we shall conclude that \hat{n} has the same eigenfunctions as H . We demonstrate that \hat{n} has as eigenvalues all the integer nonnegative numbers:

$$\hat{n}\psi_n = n\psi_n$$



1. the spectrum of \hat{n} is nonnegative (left as an exercise)
2. $\hat{n}a\psi_n = a^\dagger aa\psi_n = (aa^\dagger - 1)a\psi_n = (n - 1)a\psi_n$
3. $\hat{a}^\dagger\psi_n = (n + 1)a^\dagger\psi_n$, left as an exercise
4. $\langle a\psi_n | a\psi_n \rangle = \langle \psi_n | \hat{n} | \psi_n \rangle = n \langle \psi_n | \psi_n \rangle$
5. $\langle a^\dagger\psi_n | a^\dagger\psi_n \rangle = (n + 1) \langle \psi_n | \psi_n \rangle$

points 2,3 connote a and a^\dagger as ladder operators, i.e.

$a\psi_n = \sqrt{n}\psi_{n-1}$ and $a^\dagger\psi_n = \sqrt{n+1}\psi_{n+1}$, where the proportionality constants are deduced from points 4,5.

Since the eigenvalues must all be positive, there must be an eigenfunction of a such that $a\psi_n = 0$, hence n must be the integer sequence obtainable by repeated application of a^\dagger .



It is quite easy to calculate the eigenfunctions of H , by means either of the ladder operators or of the recursion relations they induce, however this would spoil the real advantage of the ladder operators, that is not having to deal with functions and integrals. As an example, the transition dipole $\langle \psi_n | x | \psi_m \rangle$ can be easily calculated recalling that $x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a)$ and since

$$\begin{aligned}\langle \psi_m | a^\dagger | \psi_n \rangle &= \sqrt{n+1} \delta_{m,n+1} \\ \langle \psi_m | a | \psi_n \rangle &= \sqrt{n} \delta_{m,n-1}\end{aligned}$$

we can conclude that

$$\langle \psi_m | x | \psi_n \rangle = \sqrt{\frac{\hbar}{2m\omega}} (\sqrt{n+1} \delta_{m,n+1} + \sqrt{n} \delta_{m,n-1})$$



We shall now consider the motion of 2 isolated masses moving along a single axis bound by an harmonic force. We will restrain from factoring out the center of mass motion, so that the hamiltonian:

$$H(x_1, x_2) = -\frac{\hbar^2 \nabla_1^2}{2m_1} - \frac{\hbar^2 \nabla_2^2}{2m_2} + \frac{k}{2}(x_1 - x_2)^2 = -P^\dagger \frac{M^{-1}}{2} P + X^\dagger \frac{K}{2} X$$

where we have substituted the explicit sum over particles with a matrix/vector compact notation.

As before, we need to pass to weighted coordinates:

$$\xi_i = \sqrt{m_i} x_i$$
$$\eta_i = -i\hbar \frac{d}{d\xi_i} = \frac{1}{\sqrt{m_i}} p_i$$

bringing our hamiltonian to

$$H = \frac{1}{2} \eta^\dagger \eta + \xi^\dagger \frac{D}{2} \xi$$



We have here introduced the matrix D

$$D = M^{-1/2}KM^{-1/2} = \begin{pmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} \\ -\frac{k}{\sqrt{m_1 m_2}} & \frac{k}{m_2} \end{pmatrix}$$

We now seek the eigenvalues and vectors of D , e.g. by nullifying the characteristic polynomial: $\lambda^2 - \lambda(\frac{k}{m_1} + \frac{k}{m_2}) = 0$. This yields two solutions:

$$\lambda_t = 0; \quad \xi_t = A_t \begin{pmatrix} \sqrt{m_1} \\ \sqrt{m_2} \end{pmatrix}; \quad X = A_t \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

corresponding to rigid translation, and:

$$\lambda_v = \frac{k}{\mu}; \quad \xi_v = A_v \begin{pmatrix} \sqrt{m_2} \\ \sqrt{m_1} \end{pmatrix}; \quad X = A_v \sqrt{m_1 m_2} \begin{pmatrix} \frac{1}{m_1} \\ -\frac{1}{m_2} \end{pmatrix}$$

corresponding to vibrational motion with fixed centre of mass, frequency $\omega = \sqrt{\frac{k}{\mu}}$ and amplitude A_v .



We have essentially factorized the hamiltonian into a set of independent motions:

$$H = \frac{1}{2}\eta^\dagger\eta + \xi^\dagger\frac{D}{2}\xi = -\frac{\nabla_{A_t}^2}{2m} - \frac{\nabla_{A_v}^2}{2\mu} + \frac{k}{2}A_v^2 = H_t + H_v$$

by means of which we describe displacements and solutions in terms of normal modes:

$$X \equiv \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = A_t \begin{pmatrix} 1 \\ 1 \end{pmatrix} + A_v \begin{pmatrix} \frac{1}{m_1} \\ -\frac{1}{m_2} \end{pmatrix}$$

$$\psi(X) = \phi_t(A_t)\phi_v(A_v)$$

$$H_t\phi_t(A_t) = \epsilon_t\phi_t(A_t)$$

$$H_v\phi_v(A_v) = \epsilon_v\phi_v(A_v)$$



The generalization to a generic polyatomic molecule is straightforward: from the hamiltonian

$$H = \sum \frac{p_i^2}{2m_i} + \frac{1}{2} \sum x_i k_{ij} x_j$$

we pass to weighted coordinates $\xi_i = \sqrt{m_i} x_i$:

$$H = \frac{1}{2} \eta^\dagger \eta + \xi^\dagger \frac{D}{2} \xi$$

and upon diagonalization of D arrive at new collective coordinates (normal modes), 6 of which will be degenerate roto-translation motions, (5 in the case of linear molecules) and the remaining representing independent vibration.

$$X = \sum^{3N} A_i V_i$$

where upon we factorize H into a set of $3N$ independent harmonic hamiltonians

$$H = \sum H_i(A_i)$$



Vibrations in a simple lattice

We shall analyze vibrations in the simplest lattice we can conceive, a linear lattice with a single atom cell.

First of all we shall cut a region of the crystal, because this is the simplest way to avoid infinities.

We will therefore consider N consecutive sites which, without losing generality we may number $0..N - 1$. We will also impose the Born von Karman periodicity conditions, i.e. $x_i = x_{i+N}$, so that e.g. $x_0 = x_N$.

For a better comprehension, we shall assume that each atom interacts just with its nearest neighbour by means of elastic forces, so that

$$V = \frac{k}{2} \sum_l (x_{l+1} - x_l)^2 = \frac{D}{2} \sum_l (\xi_{l+1} - \xi_l)^2$$

where we have introduced the mass weighted displacement coordinates $\xi_l = \sqrt{m}(x_l - la)$ from the equilibrium positions.



As before, the problem is that the potential couples together all the variables. We shall seek for a variable transformation that uncouples the potential function V . Such transformation is the discrete fourier transform:

$$A_m = \frac{1}{\sqrt{N}} \sum_n \xi_n e^{i\frac{2\pi}{N} mn}$$
$$A_{k=m\frac{2\pi}{Na}} = \frac{1}{\sqrt{N}} \sum_{x=na} \xi_x e^{ikx}$$

where, in the second line we have substituted the dependence on the integer m with a dependence on wavevector k , considering the displacement as a function of position (mean).

An important property of the discrete fourier transform is:

$$\frac{1}{N} \sum_n e^{i2\pi \frac{ln}{N}} e^{i2\pi \frac{mn}{N}} = \delta_{p+q}$$



Among other things, this allows us to show the inverse transform:

$$\xi_n = \frac{1}{\sqrt{N}} \sum_m A_m e^{-i2\pi \frac{mn}{N}}$$

which brings to a new expression of V :

$$\begin{aligned} V &= \frac{D}{2} \sum_n \left(\frac{1}{\sqrt{N}} \sum_m A_m e^{-i2\pi \frac{mn}{N}} - \frac{1}{\sqrt{N}} \sum_m A_m e^{-i2\pi \frac{m(n-1)}{N}} \right)^2 \\ &= \frac{D}{2N} \sum_{n,m,m'} A_m A_{m'} \left(e^{-i2\pi \frac{(m+m')n}{N}} + e^{-i2\pi \frac{(m+m')(n-1)}{N}} \right. \\ &\quad \left. - e^{-i2\pi \frac{(mn+m'(n-1))}{N}} - e^{-i2\pi \frac{(m(n-1)+m'n)}{N}} \right) \\ &= \frac{D}{2} \sum_m A_m A_{-m} (2 - e^{i2\pi \frac{m}{N}} - e^{-i2\pi \frac{m}{N}}) = \sum_m A_m A_{-m} \frac{D_m}{2} \end{aligned}$$

where $D_m = D(2 - 2\cos(2\pi m/N))$.



We apparently ended with V coupling the variables A_m and A_{-m} , however, since the displacement must be real, the constraint $A_m = A_{-m}^*$ must be satisfied, so that A_m and A_{-m} are indeed one only complex variable.

The B operators:

$$B_m = \frac{1}{\sqrt{N}} \sum_n \eta_n e^{-i2\pi \frac{mn}{N}}$$

are conjugates of the operators A_m , that is they satisfy the commutation relation $[B_m, A_n] = i\hbar\delta_{mn}$. Therefore we can finally rewrite the hamiltonian:

$$H = \frac{1}{2} \sum_n B_n^2 + D_n A_n^2$$

i.e. a sum of oscillators with angular frequency

$$\omega_m = \sqrt{D(2 - 2\cos(2\pi m/N))}.$$

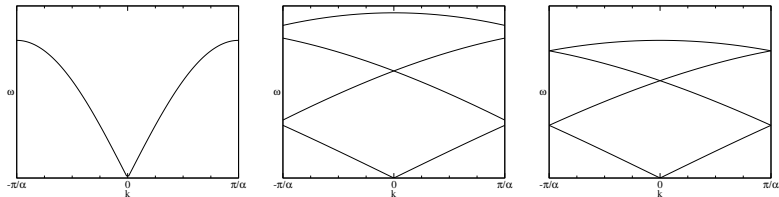


- ▶ Exercise: solve the problem with V extended to second nearest neighbour interactions.

Now, we consider a general lattice. Every cell will generally consist of M atoms, contributing so with $3M$ freedom degrees (independent displacements). Also, we will have $N = N_1 N_2 N_3$ cells, with V coupling all the $3MN$ variables.

Upon fourier transformation we arrive at a set of N independent problems, each involving $3M$ variables. Each of these problems is analogous to the problem of dynamics of an M atom molecule and brings to essentially the same solutions, except that rototranslations are substituted by motions in which all the atoms of a cell move coherently.





In simple crystals, left picture, a single curve appears in the dispersion plot. The value of $\omega(k=0)$ is always 0. The slope $\frac{d\omega}{dk}$ is the propagation speed for acoustic waves in the solid. In fact, the small k vibrations are what is perceived as sound. Actually, there are three acoustic branches, corresponding to 3 translational degrees in molecules. One of these represents longitudinal waves, the others transverse waves.

In the case of cells with more atoms, the branches are $3M$: 3 acoustic and $3M - 3$ so called optical phonons. The optical phonons are analogous of molecular vibrations and exhibit the same properties for IR excitation.



The rightmost picture, represents what happens when the cell is actually reducible. In this case, the branches exhibit degeneracy at the boundary of the Brillouin zone. Indeed the dispersion curve constitutes a "repeated representation" of the elementary cell dispersion curves.



electronic structure

The hamiltonian of a system of nuclei and electrons dictating the shape of matter, discarding relativistic and magnetic field corrections:

$$H = \sum_a h(r_a) + \sum_A h(R_A) + \frac{1}{2} \sum_{a \neq b} \frac{1}{|r_a - r_b|} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|R_A - R_B|} - \sum_{A,a} \frac{Z_A}{R_A - r_a}$$

where uppercase letters pertain to nuclear variables and lowercase letters to electronic coordinates, so that

$$h(r) = -\frac{\nabla_r^2}{2} - V(r)$$
$$h(R_a) = -\frac{\nabla_{R_a}^2}{2M_a} + Z_a V(R_a)$$

where V is an external electric field.



The electron mass is smaller than nuclear masses by a $10^3 \div 10^5$ factor, this brings to the so called Born-Hoppenheimer approximation, which amounts to factorizing the wavefunction in a product of nuclear and electronic terms.

$$\psi(R, r) = X(R)\Phi(R, r) \quad (3)$$

When Φ solves the S.E. for electrons at fixed nuclei:

$$H_e\Phi(R, r) = \epsilon(R)\Phi(R, r) \quad (\text{SE:el})$$

$$H_e = \sum_a h(r_a) + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|R_A - R_B|} - \sum_{A,a} \frac{Z_A}{|R_A - r_a|} + \frac{1}{2} \sum_{a \neq b} \frac{1}{|r_a - r_b|}$$

and $X(R)$ solves the equation:

$$\left(\sum_m h(R_m) + \epsilon(R) \right) X(R) = EX(R)$$

then:

$$HX(R)\Phi(R, r) = EX(R)\Phi(R, r) - \underbrace{X(R) \sum_A h(R_A)\Phi(R, r)}_{\text{cross diagonal}}$$



So that $X(R)\Phi(R, r)$ solves the problem of nuclear and electronic motion except for the “cross diagonal” term. The diabatic position, eq.3 requires knowing the electronic wavefunction at each nuclear position. More commonly one adopts the “adiabatic” factorization

$$\psi(R, r) = X(R)\Phi(R_0, r) \quad (4)$$

in which the electronic wavefunction pertains to fixed nuclear coordinates R_0 , usually the lowest energy configuration.

The “cross diagonal” correction term to the B.H. approximation is small but fundamental, determining the shape of the wavefunction near the crossing points of adiabatic electronic wavefunctions.



Fundamental to the computation of a many-particle wavefunction is the idea of factorizing the S.E. solution into a product of single-particle functions (orbitals).

Each electron is described by 4 variables, in real space:

$$x \equiv r, s$$

3 coordinates and a spin variable.

The tentative factorization for an n electron wavefunction:

$$\psi(x) = \prod_a \phi_a(x_a)$$

representing a system of independent electrons is not acceptable for such identical particles (fermions); for fermions the wavefunction must instead satisfy the antisymmetry relation:

$$p_{a,b}\psi(x) = -\psi(x)$$

where $p_{a,b}$ represents an operator switching the variables x_a and x_b



An antisymmetric wavefunction can “generally” be obtained from a wavefunction by means of application of an operator A

$$A = \frac{1}{N!} \sum_p \sigma_p p$$

where p are the $N!$ permutations of the N particle indexes and σ_p is the p signature, that is 1 for even permutations, -1 for odd permutations.

It is easy to see that A will zero products where the same function appears more than once and hence also any product where an orbital is a linear combination of others appearing in the same product.

The antisymmetrized product of orbitals is also called the Slater determinant.



If we now wish to calculate the energy expectation value for such a single determinant wavefunction, we have:

$$E = \frac{\langle A \prod_a \phi_a(x_a) | \sum_a h_a + \frac{1}{2} \sum_{a,b} \frac{1}{r_{ab}} | A \prod_a \phi_a(x_a) \rangle}{\langle A \prod_a \phi_a(x_a) | A \prod_a \phi_a(x_a) \rangle} \quad (5)$$

that apparently involves the summation of $N!N!N^2$ terms, clearly unmanageable for even small values of N : e.g. $10!10!10^2 > 10^{15}$. However, one can easily show that $AA = A$, i.e. A is idempotent (a projector), so that we can drop either of the A in eq.5. Moreover all the remaining products involving permutations of indexes not in the operators integrate to 0, for the canonical condition $\langle \phi_a | \phi_b \rangle = \delta_{ab}$, so that we are left only with

$$E = \sum_a \langle \phi_a | h | \phi_a \rangle + \frac{1}{2} \sum_{a,b} \langle \phi_a \phi_b | \frac{1}{r_{ab}} | \phi_a \phi_b \rangle - \frac{1}{2} \sum_{a,b} \langle \phi_a \phi_b | \frac{1}{r_{ab}} | \phi_b \phi_a \rangle$$



Now that we have all of the energy expectation value in N^2 terms, we shall attempt to minimize it, seeking for an S.E. solution through the variational principle. However we must ensure that the wavefunction be properly normalized, e.g. by means of the orthonormality condition on orbitals and we must find a convenient representation for orbitals.

The usual suspect:

$$\phi_a = \sum_{\beta} \Phi_{a\beta} B_{\beta} \quad (7)$$

ϕ_a is a linear combination of the basis B the coefficients being stored in the row a of matrix Φ .

Usually the basis is fixed and one is left with the problem of optimizing the coefficient Φ , subject to orthonormalization condition:

$$\langle \phi_a | \phi_b \rangle = \sum_{\alpha, \beta} \Phi_{a,\alpha} \Phi_{b,\beta} S_{\alpha\beta}$$

where $S_{\alpha\beta} = \langle B_{\alpha} | B_{\beta} \rangle$, the overlap matrix takes into account non orthogonality in the basis set.



The expansion in a basis set eq.7, transforms the differential S.E. into a matricial equation and the energy expectation value into:

$$E = \sum_m \Phi_m^* \mathbf{h} \Phi_m + \frac{1}{2} \sum_{m,n} (\Phi_m \Phi_n \mathbf{g} \Phi_m \Phi_n - \Phi_m \Phi_n \mathbf{g} \Phi_n \Phi_m)$$

$$\mathbf{h}_{ij} = \langle B_i | h | B_j \rangle$$

$$\mathbf{g}_{ijkl} = \langle B_i(r_1) B_j(r_2) | \frac{1}{|r_1 - r_2|} | B_k r_1 B_l r_2 \rangle$$

where \mathbf{h} and \mathbf{g} or $\mathbf{J} - \mathbf{K}$ are now matrices of expectation values over the basis set.



Also, I wish to make sure that $\langle \phi_i | \phi_j \rangle = \delta_{ij}$, which in my new representation becomes:

$$\sum_{mn} \Phi_{im} S_{mn} \Phi_{nj} = \delta_{ij}$$

so that we arrive at the lagrange function

$$\begin{aligned} L = & \sum_m \Phi_m^* \mathbf{h} \Phi_m + \frac{1}{2} \sum_{m,n} (\Phi_m \Phi_n \mathbf{g} \Phi_m \Phi_n - \Phi_m \Phi_n \mathbf{g} \Phi_n \Phi_m) \\ & + \sum_{ij} \epsilon_{ij} (\langle \Phi_i | S | \Phi_j \rangle - \delta_{ij}) \end{aligned}$$



We cannot directly solve this equation, but we can solve for:

$$\begin{aligned} L &= \sum_m \Phi_m^* \mathbf{h} \Phi_m + \frac{1}{2} \sum_{m,n} (\Phi_m \tilde{\Phi}_n \mathbf{g} \tilde{\Phi}_m \Phi_n - \Phi_m \tilde{\Phi}_n \mathbf{g} \tilde{\Phi}_n \Phi_m) \\ &+ \sum_{ij} \epsilon_{ij} (\langle \Phi_i | S | \Phi_j \rangle - \delta_{ij}) \\ &= \sum_m \Phi_m^* \mathbf{h} \Phi_m + \frac{1}{2} \sum_{m,n} \Phi_m (\mathbf{J} - \mathbf{K}) \Phi_n + \sum_{ij} \epsilon_{ij} (\langle \Phi_i | S | \Phi_j \rangle - \delta_{ij}) \end{aligned}$$

where we have substituted the unknown inner Φ in the coulomb and exchange expectation values with guessed values.



Now, making profit of some freedom in the choice of orbitals (the wavefunction does not change under unitary transformations of occupied orbitals), we can rearrange our problem:

$$L = \sum_m \Phi_m^* F \Phi_m + \sum_i \epsilon_i (\langle \Phi_i | S | \Phi_i \rangle - 1)$$

$$F = \mathbf{h} + \frac{1}{2}(\mathbf{J} - \mathbf{K})$$

$$F \Phi_i = \epsilon_i \Phi_i$$

so that we remain with a diagonalization problem. We then will use our solution for reevaluating the \mathbf{J} and \mathbf{K} matrices up to self consistency.



Analogously, for the periodic system solutions, the hartree-fock equations must be solved for at least a set of NM orbitals, where N is the number of cells comprising the supercell and M the number of orbitals spanning each cell.

However, as anticipated (Bloch theorem), the orbitals can be indexed m by m by means of N k -vectors:

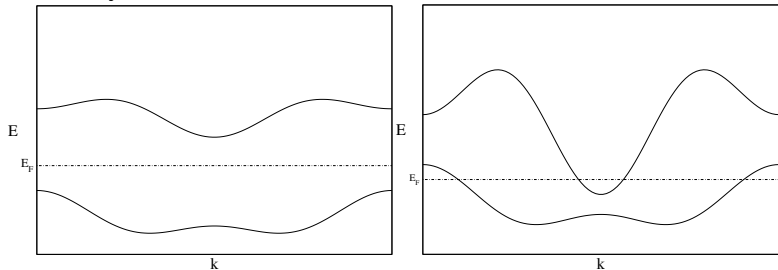
$$F\Phi_{kn} = \epsilon_{kn}\Phi_{kn}.$$

The set of energies and solutions at fixed n is called a band. Up to now, the orbitals were actually functions $\Phi(x = r, s)$, also called spinors. Actually, the most common representation of spinors is that of pure eigenstates of s_2, m_s , i.e. $\Phi = \phi_\alpha(r)\alpha$ and $\Phi = \phi_\beta(r)\beta$.

One can in many cases resort to the assumption that the spin density is 0, so that he can make the simplification $\phi_\alpha = \phi_\beta$ reducing the size of the problem (RHF). This at least requires an even number of electrons and full occupation of eventual degenerate orbitals (closed shell).



In any case one must face the problem of orbital occupation, which usually is performed in energetic order, though no general demonstration actually exists that this brings to the lowest energy for the system.



In the crystal the problem may be tougher, the bands possibly crossing near the Fermi energy, separating the occupied from the free bands at 0 K temperature.

Solids are insulators when occupied and free bands are well separated, conductors when the density of states at the Fermi energy is not null, which may happen because the unit cell has an odd number of electrons or because band spreading is larger than separation.



electron correlation

While Hartree-Fock theory is surprisingly good, correlation may make the difference in many cases. The monodeterminantal representation turns out too restrictive even in closed shell systems. In solid state, most of modern computation makes use of density functional theory, DFT, in the so called Kohn-Sham approach. The Kohn-Sham method applies the single determinant representation to both obtain n -representable densities (densities of some n electron wavefunction) and to approximate the kinetic energy of the true wavefunction as expectation values of the kinetic operator over occupied orbitals.

$$\begin{aligned} E &= T + V + C + E_{xc} \\ &= - \sum_i \langle \phi_i | \frac{\nabla^2}{2} | \phi_i \rangle + \int V(r) \rho(r) dr \\ &+ \iint \rho(r_1) \rho(r_2) \frac{1}{|r_1 - r_2|} dr_1 dr_2 + \int F_{xc}[\rho(r)] dr \end{aligned}$$

