Variational Methods for Electronic Structure

The hydrogen atom is a two-body system consisting of a proton and an electron. If spin and relativistic effects are ignored, then the Schrödinger equation for the hydrogen atom can be solved exactly. In this respect, it is similar to the Kepler problem in classical mechanics.

The classical three-body problem is nonintegrable and exact solutions exist only in very special cases. The analogous quantum mechanical system is the Helium atom, which consists of a nucleus and two electrons. This quantum mechanical problem cannot be solved exactly even if spin and relativisitic effects are ignored. The following table from the review article Rev. Mod. Phys. 72, 497-544 (2000) by Tanner et al.

TABLE I. Ground-state energies (in a.u.) of the helium atom: left, semiclassical; right, quantum-mechanical and experimental. The good agreement of the energy obtained from the Heisenberg-Sommerfeld model (see Fig. 3) must be considered as accidental (see text). The given result from Solov'ev's approach was extracted from Fig. 4 of Solov'ev (1985). The asymmetric stretch orbit (Ezra et al., 1991) is shown in Fig. 13(b), Sec. IV.B. The semiclassical cycle expansion is described in Sec. IV. The theoretical data do not include finite-mass, relativistic, or QED corrections, except for the result by Drake (1993), which contains relativistic effects. The difference between the latter result and the latest experimental figures (Bergeson et al., 1998) reflects QED effects. Some of the data are from Leopold and Percival, 1980, Table I.

	Semiclassical			Quantal/Experimental	
Year	Method	$-E$	Year	Method	$-E$
1913	orbit Fig. 2(a), Bohr (1913)	3.06	1927	first order pert. Unsöld (1927)	2.75
1919	orbit Fig. 2(c), Landé (1919)		1927	molecularlike, Slater (1927)	2.895
1921	orbit Fig. 2(b), Langmuir (1921)	2.17	1927	variational, Kellner (1927)	2.873
1921	orbit Fig. 2(d), Langmuir (1921)	2.31	1928	variational, Hylleraas (1928)	2.895
1922	"hybrid orbit," Van Vleck (1922)	2.765	1929	var., 38 param., Hylleraas (1929)	2.9037
1922	orbit Fig. 3, Heisenberg (1922)	2.904	1959	var., 38 param., Kinoshita (1959)	2.903 722
1923	orbit Fig. 2(e), Kramers (1923)	2.762	1959	perimetric coord., Pekeris (1959)	2.903 724 376
1980	1. order pert., Leopold et al. (1980)	2.7410	1988	Hylleraas type basis,	2.903 724 377
1980	variational, Leopold et al. (1980)	2.8407		Drake (1988)	03415
1985	perturb. theory, Solov'ev (1985)	3.05	1995	perimetric coordinates,	2.903 724 377
1991	as. stretch orbit, Ezra et al. (1991)	3.097		Bürgers et al. (1995)	034 119 589
1991	cycle expansion, Ezra et al. (1991)	2.932	1993	relativ. Drake (1993)	2.903 700 023
			1924	experimental, Lyman (1924)	2.9035
			1998	exp., Bergeson et al. (1998)	2.903 693 775

gives an overview of theoretical and numerical work on the Helium atom since the discovery of quantum mechanics almost 100 years ago. The ground state energy is expressed in atomic units $e = \hbar = m_e = 1$. In these units, the ground state energy of the hydrogen atom is -0.5.

The variational method for the Schroedinger equation

The variational method is used very widely in condensed matter and quantum chemistry to find energies and wavefunctions. It forms the basis for more sophisticated methods such as Hartree-Fock and density functional methods.

The variational theorem

A quantum system is described by a vector $|\psi\rangle$ in an infinite dimensional Hilbert space. If H is the energy (Hamiltonian) operator for the system, we can compute its expectation value

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \ ,$$

in various possible states $|\psi\rangle$. The *variational theorem* states that the extrema of $E[\psi]$ are eigenstates of H:

$$\delta E \equiv E[\psi + \delta\psi] - E[\psi] = 0 \qquad \Rightarrow \qquad H\psi = E\psi \ .$$

In principle we could compute the energy functional in the Hilbert space and then look for its stationary

points: these would give us the eigen energies and eigenvectors. This is not practical however because the space is infinite dimensional! It is hard enough to find a stationary point in a one-dimensional space!

The variational method looks for stationary points in a *finite dimensional subspace* of the Hilbert space. Suppose this subspace in N-dimensional. If $|\chi_p\rangle, p = 1, \ldots, N$ is a set of orthonormal *basis vectors*, i.e., unit vectors

$$\langle \chi_p | \chi_q \rangle = \delta_{pq} \ ,$$

then H can be represented by an $N \times N$ matrix $\mathbf{H}$ with elements

$$H_{pq} = \langle \chi_p | H | \chi_q \rangle \ , \quad p, q = 1, \ldots, N \ .$$

We are looking for stationary states

$$\psi = \sum_{p=1}^{N} C_p | \chi_p \rangle \ ,$$

where C_p are complex coefficients to be determined. The stationary condition becomes a matrix eigenvalue equation:

$$\mathbf{HC} = E\mathbf{C} \ , \qquad \sum_{q=1}^{N} H_{pq} C_q = E C_p \ , \quad p = 1, \ldots, N \ .$$

Let's recall some results from quantum mechanics:

- $\mathbf{H}$ is Hermitian $\mathbf{H}^\dagger = \mathbf{H}$, i.e., $H_{pq} = H_{qp}^*$. Actually in the problems we will consider, $\mathbf{H}$ is a real symmetric matrix.

- There are exactly N real eigenvalues.

- The N eigenvectors corresponding to these eigenvalues span the subspace and can be chosen to be orthonormal.

The generalized eigenvalue problem

It is actually not necessary to choose an orthonormal basis set $|\chi_p\rangle$. Any *linearly independent* set of basis vectors can be used as we will see in the examples. The eigenvalue equation for a generalized basis set is

$$\mathbf{HC} = E\mathbf{SC} \ , \qquad \sum_{q=1}^{N} H_{pq} C_q = E \sum_{q=1}^{N} S_{pq} C_q \ , \quad p = 1, \ldots, N \ .$$

where the *overlap matrix* $\mathbf{S}$ has elements

$$S_{pq} = \langle \chi_p | \chi_q \rangle \ .$$

It can be shown that

- $\mathbf{S}$ is Hermitian, and

- The eigenvalues of $\mathbf{S}$ are real and positive definite, i.e., > 0.

These properties can be used to convert the generalized eigenvalue problem to an eigenvalue problem with an orthonormal basis.

Thus the variational method is essentially a problem in *linear algebra*, i.e., the solution of linear equations involving matrices in a finite dimensional space.

The Hydrogen Atom

The Hydrogen atom is a system with two particles, electron and proton. The configuration space in which the system moves is therefore six dimensional. By moving to the center-of-mass system, the problem becomes effectively 3 dimensional, with Hamiltonian

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} ,$$

where $\mathbf{r} = \mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{p}$ is the relative coordinate of the electron with respect to the proton, e is the magnitude of the electron's charge, and $m = m_\mathrm{e}m_\mathrm{p}/(m_\mathrm{e} + m_\mathrm{p})$ is the reduced mass.

Reduction to a one-dimensional problem

By using conservation of angular motion and the fact that the ground state is spherically symmetric, i.e., it has zero orbital angular momentum, the problem can be reduced to one dimension with Hamiltonian operator

$$H = -\frac{\hbar^2}{2m}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right] - \frac{e^2}{4\pi\epsilon_0 r} ,$$

which depends on the radial coordinate r.

Exact solution for the ground state

The exact ground state energy and wavefunction are given by

$$E_0 = -\frac{e^2}{2a_0} , \qquad \psi_0(r) \sim e^{-r/a_0} .$$

where the *Bohr radius*

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} .$$

It is convenient to use *atomic units* in which $\hbar = m = e^2/(4\pi\epsilon_0) = 1$ so

$$H = -\frac{1}{2}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r}\right] - \frac{1}{r} , \qquad E_0 = -\frac{1}{2} , \qquad \psi_0(r) \sim e^{-r} .$$

Simple variational trial wave function

A simple trial wave function for the Hydrogen atom ground state is

$$\psi_{\mathrm{T},\alpha}(r) = e^{-\alpha r} .$$

The Hamiltonian acting on this function gives:

$$H\psi_{\mathrm{T},\alpha}(r) = \left[-\frac{\hbar^2\alpha^2}{2m} + \left(\frac{\hbar^2\alpha}{m} - \frac{e^2}{4\pi\epsilon_0}\right)\frac{1}{r}\right]\psi_{\mathrm{T},\alpha}(r) \equiv E(r)\psi_{\mathrm{T},\alpha}(r) .$$

The quantity $E(r)$ is called the *local energy* of the trial wavefunction. Note that choosing the variational parameter

$$\alpha = \frac{me^2}{4\pi\epsilon_0\hbar^2} = \frac{1}{a_0}$$

equal to the inverse Bohr radius makes the local energy independent of r and the trial wavefunction is proportional to the exact ground state wave function.

Linear Combination of Atomic Orbitals

Trial wavefunctions that consist of linear combinations of simple functions

$$\psi(\mathbf{r}) = \sum_n d_n \chi_n(\mathbf{r})$$

form the basis of the Linear Combination of Atomic Orbitals or LCAO method introduced by Lennard-Jones and others around 1929 to compute the energies and wavefunctions of atoms and molecules. The functions χ are chosen so that matrix elements can be evaluated analytically.

Slater orbitals using Hydrogen-like wavefunctions

$$\chi(\mathbf{r}) = Y_{\ell m}(\theta, \phi)e^{-\alpha r}$$

and Gaussian orbitals of the form

$$\chi(\mathbf{r}) = Y_{\ell m}(\theta, \phi)e^{-\alpha r^2}$$

are the most widely used forms. Gaussian orbitals form the basis of many quantum chemistry computer codes.

Because Slater orbitals give exact results for Hydrogen, we will use Gaussian orbitals to test the LCAO method on Hydrogen, following S.F. Boys, Proc. Roy. Soc. A 200, 542 (1950) and W.R. Ditchfield, W.J. Hehre and J.A. Pople, J. Chem. Phys. Rev. 52, 5001 (1970) with the basis set

$$\psi(r) = \sum_{i=0}^{N-1} d_i g_s(\alpha_i, \mathbf{r}) \ ,$$

where

$$g_s(\alpha, \mathbf{r}) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}$$

for the $\ell = 0$ s-wave states.

Because products of Gaussians are also Gaussian, the required matrix elements are easily computed:

$$S_{ij} = \int d^3r \ e^{-\alpha_i r^2} e^{-\alpha_i r^2} = \left(\frac{\pi}{\alpha_i + \alpha_j}\right)^{3/2} \ ,$$

$$T_{ij} = -\frac{\hbar^2}{2m} \int d^3r \ e^{-\alpha_i r^2} \nabla^2 e^{-\alpha_j r^2} = \frac{3\hbar^2}{m} \frac{\alpha_i \alpha_j \pi^{3/2}}{(\alpha_i + \alpha_j)^{5/2}} \ ,$$

$$V_{ij} = -e^2 \int d^3r \ e^{-\alpha_i r^2} \frac{1}{r} e^{-\alpha_j r^2} = -\frac{2\pi e^2}{\alpha_i + \alpha_j} \ .$$

The 1998 Nobel Prize in Chemistry was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry".

LCAO Codes for Hydrogen

The BFGS method can be used to minimize the variational energy.

hydrogen.py

```
from math import exp, pi, sqrt
from tools.linalg import minimize_BFGS

# physical constants
hbar = 1.0                      # Planck's constant / 2pi
m = 1.0                         # electron mass
e = 1.0                         # proton charge

# LCAO variational wave function
# psi = sum( d_i g(alpha_i, r) ) for i = 0, 1, 2, ...
# assume d_0 = 1 and vary alpha_0, d_1, alpha_1, d_2, alpha_2, ...
# vector of variational parameters
```

```
p = [ 1.0, 1.0, 0.5 ]         # initial guess for [ alpha_0, d_1, alpha_1 ]
N = int( (len(p) + 1) / 2 ) # number of Gaussians

accuracy = 1.0e-6              # desired accuracy for numerical operations

def g(alpha, r):              # normalized s-wave Gaussian orbital
    return (2.0 * alpha / pi)**(3.0/4.0) * exp(-alpha * r**2)

def Sij(alpha_i, alpha_j):  # matrix elements of S
    return (pi / (alpha_i + alpha_j))**(3.0/2.0)

def Tij(alpha_i, alpha_j):  # matrix elements of T
    return (3.0 * hbar**2 / m * alpha_i * alpha_j *
            pi**(3.0/2.0) / (alpha_i + alpha_j)**(5.0/2.0))

def Vij(alpha_i, alpha_j):  # matrix elements of V
    return - 2.0 * e**2 * pi / (alpha_i + alpha_j)

def E(alpha, d):              # energy as function of N alpha_i and d_i
    S = H = 0.0
    for i in range(len(alpha)):
        for j in range(len(alpha)):
```

```
            fac = (alpha[i] * alpha[j])**(3.0/4.0)* d[i] * d[j]
            H += fac * (Tij(alpha[i], alpha[j]) + Vij(alpha[i], alpha[j]))
            S += fac * Sij(alpha[i], alpha[j])
    return H / S

def func(p):                    # function for BFGS minimization
    # assume p = [ alpha_0, d_1, alpha_1, d_2, alpha_2, ... ]
    alpha = [ max(p[2 * i], accuracy) for i in range(N) ]
    d = [ 1.0 ]
    d.extend(p[2 * i + 1] for i in range(N - 1))
    return E(alpha, d)

def dfunc(p, g):                # gradient of func for BFGS minimization
    # use symmetric finite difference f'(x) = (f(x+eps) - f(x-eps)) / (2 eps)
    eps = 0.5 * accuracy     # finite difference
    for i in range(len(p)):
        p1 = list(p)
        p1[i] += eps
        p2 = list(p)
        p2[i] -= eps
        g[i] = (func(p1) - func(p2)) / (2 * eps)
    return
```

```
def norm(p):                    # norm of LCAO
    alpha = [ p[2 * i] for i in range(N) ]
    d = [ 1.0 ]
    d.extend(p[2 * i + 1] for i in range(N - 1))
    norm = 0.0
    for i in range(N):
        for j in range(N):
            norm += Sij(alpha[i], alpha[j]) * d[i] * d[j]
    return sqrt(norm)

print(" Variational method for Hydrogen using Gaussian LCAO")
print(" Minimize <psi|H|psi>/<psi|psi> using BFGS algorithm")
gtol = accuracy
iterations, e = minimize_BFGS(p, gtol, func, dfunc)
print(" number of Gaussians N = " + repr(N))
print(" number of iterations = " + repr(iterations))
print(" energy E = " + repr(e))
print(" i\talpha_i\t\t\td_i")
exit
for i in range(N):
    alpha_i = p[2 * i]
```

```
    if i == 0:
        d_i = 1.0 / norm(p)
    else:
        d_i = p[2 * i - 1] / norm(p)
    print(" " + repr(i) + "\t" + repr(p[2*i]) + "\t" + repr(d_i))
```

The Helium Atom

The Helium atom is a 3-particle problem: two electrons orbit around a nucleus, which consists of two protons with charge e each and two neutral neutrons. The nucleus, which is $\sim 8,000$ times more massive than an electron, can be assumed to be at rest at the origin of the coordinate system. The electrons have positions $\mathbf{r}_1$ and $\mathbf{r}_2$. This is simpler than making a transformation to the center-of-mass system of the three particles, and it is sufficiently accurate.

If we use atomic units with $\hbar = m_e = e = 1$, the Hamiltonian for the motion of the two electrons can be written

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \, ,$$

where

$$r_{12} = |\mathbf{r}_{12}| = |\mathbf{r}_1 - \mathbf{r}_2| \, .$$

The terms $-2/r_i$ represent the negative (attractive) potential energy between each electron with charge -1 and the Helium nucleus with charge $+2$, and the term $+1/r_{12}$ represents the positive (repulsive) potential

energy between the two electrons.

A simple choice of variational trial wave function

If the repulsive term $1/r_{12}$ were not present, then the Hamiltonian would be that of two independent Hydrogen-like atoms. It can be shown that the energy and ground state wave function of a Hydrogen-like atom whose nucleus has charge Z are given by

$$E_0 = -\frac{Z^2}{2} \, , \qquad \psi_0 \sim e^{-Zr} \, .$$

The wave function of the combined atom with two non-interacting electrons would be the product of two such wave functions:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) \sim e^{-2r_1}e^{-2r_2} \, .$$

This suggests a trial wave function of the form

$$\Psi_{\mathrm{T},\alpha} = e^{-\alpha r_1}e^{-\alpha r_2} \, ,$$

similar to what was done for the Hydrogen atom. If the electron-electron interaction is neglected, then the average energy with this wave function can be calculated

$$\left\langle -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \right\rangle = 2 \times \frac{\alpha^2}{2} - 2 \times 2 \times \alpha \, ,$$

which has a minimum at $\alpha = 2$, which gives $\langle E \rangle = -4$. The experimentally measured ground state energy is $E_0 = -2.904$.

In fact, the average energy can be evaluated exactly for this trial wave function even if the electron-electron interaction is included:

$$\left\langle -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right\rangle = \alpha^2 - \frac{27}{8}\alpha \ ,$$

which has a minimum at $\alpha = 27/16$, which gives $\langle E \rangle = -2.8477$. This shows that the electron-electron interaction is important, and including it gives remarkably good agreement with the experimental value.

Variational Calculations of Hylleraas and others

The variational method for the Helium atom using Slater orbitals with multiple variational parameters was pioneered by E.A. Hylleraas in *Z. Phys.* 48, 469 (1929). He used a variational wave function

$$\psi = e^{-ks/2}\left(1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2\right) \ ,$$

where the variables

$$s = r_1 + r_2 \ , \qquad t = r_2 - r_1 \ , \qquad u = r_{12}$$

were chosen to deal with singularities in the potential energy. Minimizing the energy by varying $k, \beta, \gamma, \delta, \epsilon, \zeta$, he found the value

$$E_0 = -2.90324 \text{ a.u.}$$

for the ground state energy of the Helium atom.

Chandrasekhar, Elbert and Herzberg Phys. Rev. 91, 1172 (1953) improved on Hylleraas' calculation by using 9 parameters

$$e^{-ks/2}\left(1 + \beta u + \gamma t^2 + \delta s + \epsilon s^2 + \zeta u^2 + \chi_6 su + \chi_7 t^2 u + \chi_8 u^3 + \chi_9 t^2 u^2\right)$$

and found

$$E_0 = -2.903603 \text{ a.u.}$$

Numerous other variational calculations have since been performed, one of the most recent being by V.I. Korobov Phys. Rev. A 66, 024501 (2002) who used 5200 variational parameters and obtained

$$E_0 = -2.903724377034119598311159 \text{ a.u.}$$

The review article by G.W.F. Drake, Physica Scripta, T83, 83 (1999) summarizes experimental and theoretical work on the Helium atom since the early calculations of Hylleraas.

Evaluation of Matrix Elements

The expectation value of the energy in the variational state can be evaluated analytically using formulas in Wikipedia: Slater type orbital.

Self Consistent Field Methods for Electronic Structure

Self Consistent Field (SCF) methods were introduced by Hartree, and developed by Slater, Fock and others in the late 1920s to study the electronic structure of atoms with more than one electron. These "Hartree-Fock" methods are widely used to compute properties of atoms, molecules and solids.

The two basic approximations in this method are to treat the atomic nuclei as infinitely heavy and therefore fixed in space at their equilibrium positions, and to approximate the many electron wavefunction as a product of one-electron wave functions that is fully antisymmetrized because electrons are fermions which must obey the Pauli exclusion principle.

The simplification achieved by these approximations is to replace the many-electron Schroedinger equation with an effective one-electron Schroedinger equation for a particle moving in an effective Coulomb potential determined by the wavefunctions of all the other electrons.

The Born Oppenheimer Approximation

The Born-Oppenheimer approximation takes the wavefunction of an atom or molecule to be the product

$$\Psi = \psi_{\text{electrons}}\psi_{\text{nuclei}}$$

of independent wavefunctions for the electrons and the much heavier nuclei.

The electron wavefunction obeys an approximate many-electron Schroedinger equation with Hamiltonian

$$H_{\text{B-O}} = \sum_i \frac{\mathbf{p}_i^2}{2m} + \frac{1}{4\pi\epsilon_0}\sum_{i=0}^{N-2}\sum_{j=i+1}^{N-1}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0}\sum_i\sum_k\frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_k|} \,,$$

where $\mathbf{r}_i, \mathbf{p}_i$ are the position and momentum operators of the electrons, and $Z_k, \mathbf{R}_k$ are the nuclear charge and classical position variable of the k-th nucleus.

For the Helium atom $Z = 2$ and the nucleus is assumed fixed at the origin $\mathbf{R} = 0$ of the electron coordinate system. For the Hydrogen molecule $Z = 1$ and R_k are taken to be fixed equilibrium positions of the two protons in the ground state of the molecule.

Slater Determinant for the Many Electron Wavefunction

Because electrons are fermions and obey the Pauli exclusion principle, the many electron wavefunction must be antisymmetric under exchange of any two electrons.

This property is absolutely essential to reproduce the observed shell structure of atomic electrons and the Fermi surface of electrons in metals.

The position and spin of the i-th electron can be represented by the combined variables

$$\mathbf{x}_i = \{\mathbf{r}_i, s_i\}$$

where s_i is the spin quantum number of the electron along a quantization direction (conventionally chosen to be the z axis).

The Slater determinant is a product-form approximation to the many-electron wavefunction in which the N electrons are in N different quantum states described by single electron wavefunctions ψ_j

$$\psi(\mathbf{x_0}, \mathbf{x_1}, \ldots, \mathbf{x_{N-1}}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_0(\mathbf{x}_0) & \psi_1(\mathbf{x}_0) & \cdots & \psi_{N-1}(\mathbf{x}_0) \\ \psi_0(\mathbf{x}_1) & \psi_1(\mathbf{x}_1) & \cdots & \psi_{N-1}(\mathbf{x}_1) \\ \vdots & \vdots & \vdots & \\ \psi_0(\mathbf{x}_{N-1}) & \psi_1(\mathbf{x}_{N-1}) & \cdots & \psi_{N-1}(\mathbf{x}_{N-1}) \end{vmatrix} .$$

Self Consistent Field Method for the Ground State of the Helium Atom

If relativistic spin-orbit couplings are neglected, the single electron wavefunctions can be taken to be products of spin and orbital terms. Because there are only two electrons, the approximate ground state wavefunction is antisymmetric in spin with both electrons in the same orbital state

$$\psi(\mathbf{x_0}, \mathbf{x_1}) = \phi(\mathbf{r}_0)\phi(\mathbf{r}_1) \left[\frac{|\uparrow\rangle_0| \downarrow\rangle_1 - |\downarrow\rangle_0| \uparrow\rangle_1}{\sqrt{2}} \right] .$$

The time-independent two-electron Schroedinger equation in the Born-Oppenheimer approximation becomes

$$\left[-\frac{1}{2}\nabla_0^2 - \frac{1}{2}\nabla_1^2 - \frac{2}{r_0} - \frac{2}{r_1} + \frac{1}{r_{01}} \right] \phi(\mathbf{r}_0)\phi(\mathbf{r}_1) = E\phi(\mathbf{r}_0)\phi(\mathbf{r}_1) .$$

This equation is nonlinear in the unknown function $\phi(\mathbf{r})$. It is also non-local because it involves two points in space. The electron-electron interaction term prevents us from separating the equation into two local linear equations.

To solve this difficult problem Hartree suggested starting from a partially linearized equation obtained by multiplying both sides on the left by $\phi(\mathbf{r}_1)$ and integrating over all space in the the variables $\mathbf{r}_1$ to obtain

$$\left[-\frac{1}{2}\nabla_0^2 - \frac{2}{r_0} + \int d^3\mathbf{r}_1 \frac{|\phi(\mathbf{r}_1)|^2}{|\mathbf{r}_0 - \mathbf{r}_1|} \right] \phi(\mathbf{r}_0) = E'\phi(\mathbf{r}_0) ,$$

where the third integral term on the left is the Coulomb energy of the first electron in the field due to the charge density of the second, and the shifted eigenvalue

$$E' = E + \frac{1}{2}\int d^3\mathbf{r} \ \phi(\mathbf{r})\nabla^2\phi(\mathbf{r}) + 2\int d^3\mathbf{r} \frac{\phi(\mathbf{r})^2}{r} ,$$

differs from ground state energy E by a constant factor independent of $\mathbf{r}_0$.

The transformed equation looks like a one-particle Schroedinger equation with an additional integral contribution that depends on the solution we are trying to find.

To solve this equation Hartree suggested using a self-consistent iterative procedure:

- ■ Start with a reasonable guess for $\phi(\mathbf{r})$.

  - • Use this guess to evaluate the integral, which now serves as a "potential" energy $V(\mathbf{r}_0)$.
  - • Solve this linear Schroedinger equation to obtain an improved wavefunction $\phi_{\mathrm{improved}}(\mathbf{r})$.

■ Repeat the above steps with $\phi = \phi_{\mathrm{improved}}$ until a self-consistent wavefunction is obtained.

Approximate Solution Using a Linear Combination of Atomic Orbitals

To solve the Hartree equation self-consistently, the unknown continuous function $\phi(\mathbf{r})$ must be approximated by a discrete set of unknown real numbers.

Variational LCAO wavefunctions provide a very convenient and widely used discretization. Slater-type orbitals (STO) are most familiar from atomic physics. Gaussian-type orbitals (GTO) are more appropriate for molecular problems and are very widely used in quantum chemistry software packages.

A Simple GTO Parametrization for the Helium Atom

Consider a GTO parametrization

$$\phi(\mathbf{r}) = \sum_{p=0}^{L-1} c_p \chi_p(r) = \sum_{p=0}^{P-1} c_p e^{-\alpha_p r^2} \, ,$$

which parametrizes the unknown wavefunction using PL real numbers $c_p, \alpha_p, p = 0, 1, \ldots, P-1$, to be determined by iterative solution of the Hartree equation.

Using Published GTO Basis Sets

To perform a full self-consistent calculation to determine all $2P$ parameters is complicated because the α_p occur in the Gaussian exponents. Most practical calculations make use of values in published Basis sets.

The following code uses four angular momentum $\ell = 0$ or s-wave Gaussians

$$\phi(\mathbf{r}) = \sum_{p=0}^{3} c_p e^{-\alpha_p r^2} \, ,$$

and published values for $P = 4$ exponential coefficients

$$\alpha_0 = 0.297104 \, , \qquad \alpha_1 = 1.236745 \, , \qquad \alpha_2 = 5.749982 \, , \qquad \alpha_3 = 38.216677 \, ,$$

and determines the 4 prefactor coefficients c_0, c_1, c_2, c_3. This avoids the full nonlinear optimization required to determine all 8 coefficients self-consistently.

Self-Consisten Field Code for the Helium Atom

The single-particle Hartree-Fock equation for $\phi(\mathbf{r})$ is

$$\left[-\frac{1}{2}\nabla^2 - \frac{2}{r} + \sum_{r,s} c_r c_s \int d^3\mathbf{r}' \frac{\chi(\mathbf{r}')\chi(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \sum_q c_q \chi_q(\mathbf{r}) = E' \sum_q c_q \chi_q(\mathbf{r}) \, .$$

Multiply on the left with $\chi(\mathbf{r})$ and integrate to reduce it to a 4×4 matrix equation

$$\sum_{p,q} \left[h_{pq} + \sum_{rs} c_r c_s Q_{pqrs} \right] c_q = E' \sum_{pq} S_{pq} c_q$$

where

$$h_{pq} = \left\langle \chi_p \left| -\frac{1}{2}\nabla^2 - \frac{2}{r} \right| \chi_q \right\rangle = \frac{3\alpha_p \alpha_q \pi^{3/2}}{(\alpha_p + \alpha_q)^{5/2}} - \frac{2\pi e^2}{\alpha_p + \alpha_q} ,$$

$$S_{pq} = \langle \chi_p | \chi_q \rangle = \left(\frac{\pi}{\alpha_p + \alpha_q} \right)^{3/2} ,$$

and

$$Q_{pqrs} = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \chi_p(\mathbf{r}_1)\chi_r(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\chi_q(\mathbf{r}_1)\chi_s(\mathbf{r}_1)$$

$$= \frac{2\pi^{5/2}}{(\alpha_p + \alpha_q)(\alpha_r + \alpha_s)\sqrt{\alpha_p + \alpha_q + \alpha_r + \alpha_s}} .$$

Iterative Algorithm to Solve the Hartree-Fock Equation

The matrix equation for the unknown prefactor coefficient vector $\mathbf{C} = \{c_0, c_1, c_2, c_3\}$ is not linear, so it is solved iteratively.

- Choose an initial $\mathbf{C}$, for example $\mathbf{C} = \frac{1}{\sqrt{4}}\{1, 1, 1, 1\}$

- Compute the 4×4 matrix coefficients h_{pq} and S_{pq} and the $4 \times 4 \times 4 \times 4$ matrix coefficients Q_{pqrs}.
- Construct a 4×4 matrix $\mathbf{A}$ with coefficients

$$A_{pq} = h_{pq} + \frac{\sum_{rs} Q_{pqrs} c_r c_s}{\sum_{rs} c_r S_{rs} c_s} .$$

- Solve the generalized eigenvalue problem

$$\mathbf{A}\,\mathbf{C} = E'\mathbf{S}\,\mathbf{C}$$

for the eigenvector corresponding to the lowest eigenvalue.

- Repeat the steps above using the eigenvector corresponding to the lowest eigenvalue until a self-consistent solution is obtained within the desired accuracy.

- The ground state energy is given by

$$E = 2\sum_{pq} c_p c_q h_{pq} + \sum_{pqrs} Q_{pqrs} c_p c_q c_r c_s .$$

Density Functional Theory of Electronic Structure

Variational and Self Consistent Field (Hartree-Fock) methods approximate the N-electron wavefunction by a linear combination of Slater determinants. Each determinant is an antisymmetrized sum of products of N single electron orbital functions. By using a sufficient number of orbitals and variational parameters, the ground state energy can be computed for small atoms and molecules to any number of significant figures that can be measured experimentally. However, the computational resources required increase exponentially with atomic number Z for atoms and number of atomic nuclei for molecules for any method based on Slater determinants. These methods are inefficient for large molecules and many electrons, and they have not been widely used to study solids.

The Density Functional Approach

The most successful method for studying the electronic structure of atoms, molecules and solids was formulated by Hohenberg and Kohn Phys. Rev. 136, B864-B871 (1964) and Kohn and Sham Phys. Rev. 140, A1133-A1138 (1965).

To quote Walter Kohn's Nobel Lecture

"Theoretical chemists and physicists, following the path of the Schroedinger equation, have bcome accustomed to think in a truncated *Hilbert space of single particle orbitals*. DFT provides a complementary perspective. It focuses on the quantities in the real 3-dimensional coordinate space, principally on the elec-

tron density $n(\mathbf{r})$ of the ground state. These quantities are *physical*, independent of representation, and easily *visualizable* even for very large systems."

The figure from Kohn's lecture shows an application by E. Nusterer, P.E. Bloechl and K. Schwarz, "Structure and Dynamics of Methanol in a Zeolite", Angew. Chem. 35, 175-177 (1996)

S. Kotochigova, Z.H. Levine, E.L. Shirley, M.D. Stiles, and C.W. Clark, "Local-density-functional calculations of the energy of atoms," Phys. Rev. A 55, 191-199 (1997) use DFT to compute the ground state energies of every atom in the periodic table to 6 significant figures.　　　　　　　　　　　　　　　　junk

```
Helium
  2       He       1s2
                 LDA              LSD             RLDA            ScRLDA

Etot  =      -2.834836        -2.834836       -2.834785       -2.834785
Ekin  =       2.767922         2.767922        2.767773        2.767751
Ecoul =       1.996120         1.996120        1.996036        1.996030
Eenuc =      -6.625564        -6.625564       -6.625496       -6.625471
Exc   =      -0.973314        -0.973314       -0.973098       -0.973096

       1s    -0.570425        -0.570425       -0.570345       -0.570348
                              -0.570425
```

http://physics.nist.gov/PhysRefData/DFTdata/Tables/02He.html
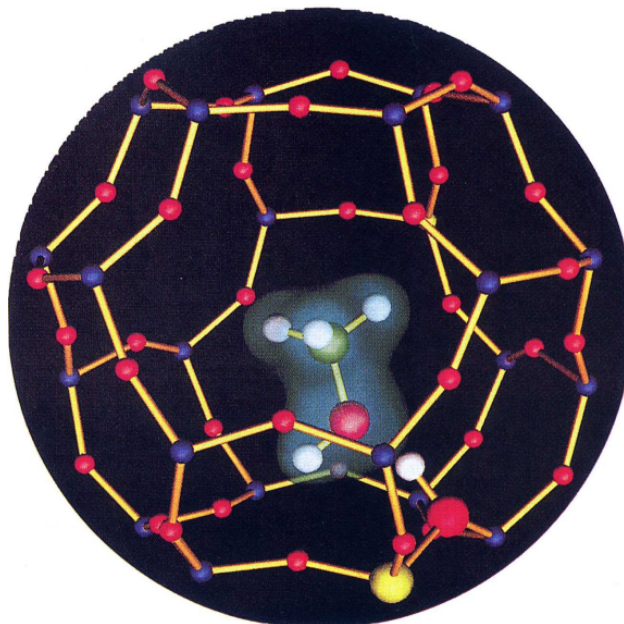
Walter Kohn   215

Figure 1. Methanol inside a cage of the zeolite sodalite. Zeolites are crystalline arrays of cages built of silicon (blue), aluminum (yellow), and oxygen (red) atoms. For each *Al* atom one must have a positive counter-ion (in this case *H⁺* (white)). A methanol molecule is inside the cage (carbon is green) where it can react with the proton. DFT calculations have assigned and clarified the IR spectra, have determined the binding sites of methanol, and have calculated the activation energy for the reaction. Acid catalysis in zeolites is widely used in the chemical industry. (After E. Nusterer, P. Bloechl and Karlheinz Schwarz, Angew. Chem. **35**, 175).

The Thomas-Fermi Model and Dirac Exchange Energy

L.H. Thomas Proc. Cambridge Philos. Soc. 23, 542-548 (1927) and E. Fermi, Rend. Accad. Naz. Lincei 6, 602-607 (1927) proposed the Thomas-Fermi model to compute the electronic properties on atoms with many electrons using the average electron density $n(\mathbf{r})$ as the basic variable in place of the many-electron Schroedinger wavefunction $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$.

They expressed the ground state energy of the system in the form

$$E_{\mathrm{TF}} = \frac{3}{10}(3\pi^2)^{2/3} \int d^3\mathbf{r} \, [n(\mathbf{r})]^{5/3} + \int d^3\mathbf{r} \, v_{\mathrm{ext}}(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \; .$$

The first term represents the kinetic energy of the electrons, the second the energy of interaction with the Coulomb potential of the atomic nucleus considered to be an "external" field, and the third term is obviously the electron-electron Coulomb interaction energy.

P.A.M. Dirac, "Note on Exchange Phenomena in the Thomas Atom" Proc. Cambridge Philos. Soc., 26, 376-385 (1930) added an additional contribution to the energy due to electron exchange effects

$$E_{\mathrm{x}} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d^3\mathbf{r} \, [n(\mathbf{r})]^{4/3} \; .$$

Density Function Theory is also based on the electron density as a fundamental variable, combining it with the basic strategy of self consistent mean field theory to replace the many electron Schroedinger equation with a one-electron equation.

The Hohenberg-Kohn Theorems

Two basic theoretical results were discovered by P. Hohenberg and W. Kohn, "Inhomogeneous Electron Gas", Phys. Rev. 136, B864-B871 (1964)

Theorem 1: The external potential $v_{\text{ext}}(\mathbf{r})$, and hence the total energy, is a unique functional of the electron density $n(\mathbf{r})$.

Theorem 2: The ground state energy $E[n(\mathbf{r})]$ can be obtained variationally: the density that minimizes the total energy is the exact ground state density.

The Kohn-Sham Equations

W. Kohn and L.J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects", Phys. Rev. 140, A1133-A1138 (1965) used the Hohenberg-Kohn theorems to derive an equivalent exact Schroedinger equation The density functional approach abandons Slater determinants of electron orbitals, which are complicated functions of N position variables $\mathbf{r}_j$ in a $3N$ dimensional configuration space, and uses instead the density of electrons

$$n(\mathbf{r}) = \sum_{k=1}^{N} |\psi_k(\mathbf{r})|^2$$

where the wavefunctions ψ_j are the N lowest energy eigenfunctions of a single-particle Schroedinger equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}) \ ,$$

where

$$v_{\text{KS}}(\mathbf{r}) = -\sum_{\ell=1}^{L} \frac{Z_\ell}{|\mathbf{r} - \mathbf{R}_\ell|} + \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

$Z_\ell, \mathbf{R}_\ell$ are the atomic number and position vectors in the Born-Oppenheimer approximation of L atomic nuclei, and $v_{\text{xc}}(\mathbf{r})$ is the exchange correlation potential, which is a functional of the electron density.

The exchange correlation potential represents the correction to a self consistent field approximation which includes the electron kinetic energy, the Coulomb potential energy due to the atomic nuclei, and the Hartree potential energy due to the other electrons.

The sum of these four contributions gives the exact ground state energy. The exchange correlation potential is defined implicitly by the functional derivative

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})} \left[E[n(\mathbf{r})] - \left\langle -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) \right\rangle \right] = \frac{\delta}{\delta n(\mathbf{r})} E_{\text{xc}}[n(\mathbf{r})] \ .$$

The Local Density Approximation to the Kohn-Sham Equations

Kohn and Sham also suggested a simple approximation that allows the exact KS equations to be solved numerically.

The problem is that the exchange correlation potential $v_{\mathrm{xc}}(\mathbf{r})$ is a *functional* of the electron density, i.e., it depends not just on the value of the density at the local point $\mathbf{r}$ in space but on the density *everywhere* inside the atom.

The approximation is to assume that the electron density is slowly varying in space. If the density were exactly constant then $v_{\mathrm{xc}}(\mathbf{r})$ would be determined by this constant value

$$E_{\mathrm{xc}}[n(\mathbf{r})] = \int d^3\mathbf{r}\; \varepsilon_{\mathrm{xc}}[n(\mathbf{r})]\; [n(\mathbf{r})]$$

The properties of a uniform homogeneous electron gas, also called Jellium, can be studied exactly. The electrons in jellium are assumed to move in a uniform static background positive charge density distribution so that the whole system is neutral. The electrons interact with one another via Coulomb forces. The electrons are fully quantum mechanical and obey the Pauli exclusion principle taking spin into account. The average volume occupied by an electron is determined by the *electron radius*

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$$

and the local part of the exchange energy of jellium can be calculated exactly

$$\varepsilon_{\mathrm{xc}}(\mathbf{r}) = -\frac{3}{4}\left(\frac{3}{\pi}[n_\uparrow + n_\downarrow]\right)^{1/3} = -\frac{3}{4}\left(\frac{3}{2\pi}\right)^{2/3}\frac{1}{r_s} = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}[n(\mathbf{r})]^{1/3}\;.$$

Iterative Algorithm to solve the LDA Equations

■ Start with an initial guess for the electron density $n(\mathbf{r})$.

　• Evaluate the Kohn-Sham potential $v_{\mathrm{KS}}[n(\mathbf{r})]$.

　• Solve the Kohn-Sham one-electron Schroedinger equation numerically and find the N lowest eigenfunctions and corresponding eigenvalues.

　• Calculate the new electron density by occupying the energy levels according to the Pauli exclusion principle.

■ Compute the ground state energy using this new electron density.

■ Repeat the steps above until convergence is achieved to the desired number of significant figures.

Density Functional Method for the Helium Atom

The two electrons in the Helium atom are assumed to occupy spherically symmetric $1s$ orbital states. The Pauli Principle is satisfied if the spin wave function is an antisymmetric singlet state.

<div align="right">helium-dft.py</div>

```
# A Density Functional Program for the Helium Atom
# Thijssen, Chapter 5, Section 5.5 and Problem 5.3
```

Solving the Radial Schrödinger Equation

The radial Schrödinger equation for the Hydrogen atom in atomic units is

$$\left[-\tfrac{1}{2}\nabla^2 - \frac{1}{r}\right] u(r) = Eu(r) , \quad u(r) = rR(r) \propto re^{-r} , \quad E = -0.5 .$$

For the Helium atom we need to solve the radial Kohn-Sham equation

$$\left[-\tfrac{1}{2}\nabla^2 - \frac{2}{r} + V_{\mathrm{H}}(r) + V_{\mathrm{x}}(r) + V_{\mathrm{c}}(r)\right] u(r) = \epsilon u(r) ,$$

where $V_{\mathrm{H,x,c}}$ are the Hartree, exchange, and correlation potentials.

Electronic Structure of Crystalline Solids

Computing the electronic structure of electrons in solid materials (insulators, conductors, semiconductors, superconductors) is in general a very difficult problem because of the large number of ions and electrons.

Many of the computational methods used to study solids can be illustrated on the simple and technologically important examples of copper and silicon.
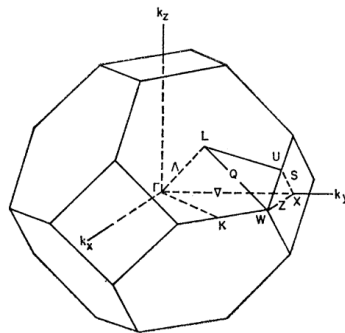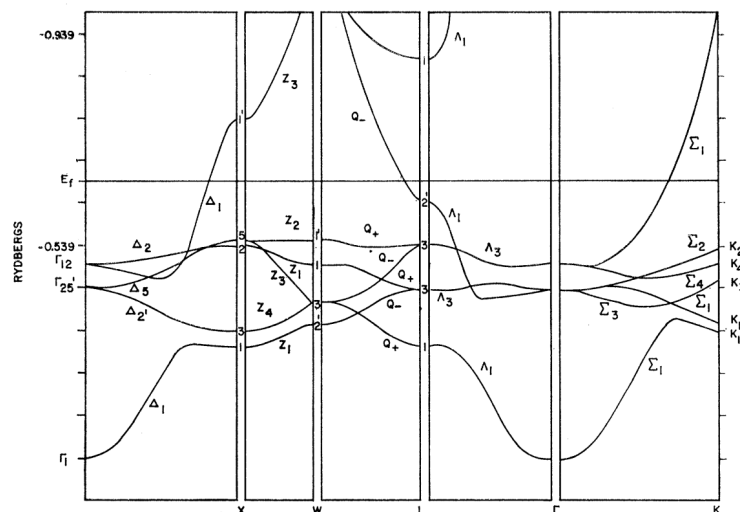
Band Structure

FIG. 2. The Brillouin zone for the face-centered cubic lattice.

In a crystalline solid the problem is greatly simplified by using Bloch's Theorem, which essentially reduces

the number of degrees of freedom to those in a single unit cell of the lattice, or a single Brillouin zone of the reciprocal lattice. The figure above from G.A. Burdick, "Energy Band Structure of Copper", Phys. Rev. 129, 138-150 (1963) shows the Brillouin zone of Copper, and the figure below shows the calculated band structure.

Copper has a face centered cubic lattice structure, which we also encountered in MD simulation of Argon atoms. A neutral copper atom has 29 electrons, 18 in an innermost Argon like core, $2 \times (2 \times 2 + 1) = 10$ in

a completely filled d $(L = 2)$ shell, and one electron in the outermost s shell. In metallic copper the 28-electron ion cores form an FCC lattice and the $4s$ shell electrons from each atom contribute to a conduction band.

The Kronig-Penney Model

The Kronig-Penney model is a simple one-dimensional model that illustrates the formation of energy bands and gaps for a Particle in a periodic potential.

Lattice periodicity

Consider a simple one-dimensional model of a crystal. N heavy nuclei at fixed at lattice sites with lattice spacing a. The much lighter atomic electrons move in a potential $V(x)$ due to the fixed lattice of ions.
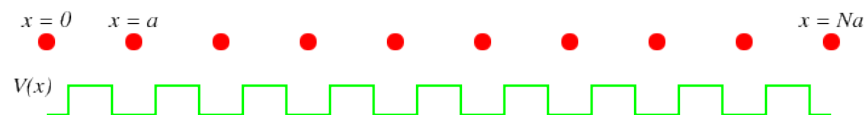
The figure shows a simple model of the potential seen by a conduction electron in a one-dimensional crystal. This is a crude approximation to the Coulomb forces: a periodic finite square well potential that is attractive near the nuclei.

To make the problem well-defined, we need to specify what happens at the boundaries $x = 0$ and $x = Na$ of the lattice. Periodic boundary conditions best approximate an macroscopically large (infinite) crystal. We suppose that all functions of x are periodic, i.e., $f(x + Na) = f(x)$.

Reciprocal space

It is useful to be able to work in momentum (or wave-number) space and expand functions of x in a Fourier series

$$f(x) = \sum_k e^{ikx} f_k \ ,$$

where f_k are Fourier coefficients. Periodic boundary conditions restrict the possible values of k:

$$e^{ik(x+Na)} = e^{ikx} \quad \Rightarrow \quad k = \frac{2\pi n}{Na} \ , \text{ where } n = 0, \pm 1, \pm 2, \ldots$$

The crystal lattice can be generated by taking a lattice point and translating it by a vector

$$\mathbf{R} = n\mathbf{a} \ , \text{ where } \mathbf{a} = a\hat{x} \ , \text{ and } n = 0, \pm 1, \pm 2, \ldots,$$

where $\hat{x}$ is a unit vector in the $+x$ direction. The vector $\mathbf{a}$ is a basis vector of the lattice, and it defines a

unit cell. The reciprocal lattice is similarly defined by a basis vector $\mathbf{b}$ which satisfies

$$\mathbf{a} \cdot \mathbf{b} = 2\pi \quad \text{that is} \quad \mathbf{b} = (2\pi/a)\hat{x} \ .$$

The reciprocal lattice points are given by the wave vectors

$$\mathbf{K} = n\mathbf{b} \ , \quad \text{where } n = 0, \pm 1, \pm 2, \ldots$$

The wavenumbers k that are smaller in magnitude than $\frac{1}{2}b = \frac{\pi}{a}$ constitute the first Brillouin zone:

$$k = 0, \pm \frac{2\pi}{Na}, \pm \frac{4\pi}{Na}, \pm \frac{6\pi}{Na}, \ldots \pm \frac{(N-1)\pi}{Na}, \frac{\pi}{a} \ .$$

A general wave number q can be decomposed into a wave number k in the first Brillouin zone, and a wave number of the reciprocal lattice

$$q = k + K \ .$$

Bloch's theorem

Since the lattice potential $V(x)$ is periodic, it can be expanded in a Fourier series

$$V(x) = \sum_K e^{iKx} V_K \ ,$$

over the reciprocal lattice vectors $\mathbf{K}$. The wave function of an electron in an energy eigenstate obeys

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x) \ .$$

Expand ψ in a Fourier series

$$\psi(x) = \sum_q e^{iqx} C_q = \sum_{K,k} e^{i(k+K)x} C_{k+K} \ ,$$

and plug into Schroedinger's equation using units in which $\hbar^2/m = 1$

$$\sum_{K,k} \left\{ \left[\frac{1}{2}(k+K)^2 - E \right] e^{i(k+K)x} C_{k+K} \right\}$$

$$+ \sum_{K'} V_{K'} \sum_{K,k} e^{i(k+K+K')x} C_{k+K} = 0 \ .$$

Since K and K' are both reciprocal lattice vectors, we can make a change of summation variable $K + K' \rightarrow K$:

$$\sum_{K,k} e^{i(k+K)x} \left\{ \left[\frac{1}{2}(k+K)^2 - E \right] C_{k+K} + \sum_{K'} V_{K-K'} C_{k+K'} \right\} = 0 \ .$$

Since the Fourier functions $e^{iqx} = e^{i(k+K)x}$ are linearly independent,

$$\left[\frac{1}{2}(k+K)^2 - E \right] C_{k+K} + \sum_{K'} V_{K-K'} C_{k+K'} = 0 \ .$$

This is very interesting: it shows that modes C_{k+K} with different wave numbers k in the first Brillouin zone decouple from one another! Another way of stating this is to note that the eigenstates of the system are of the form

$$\psi_k(x) = e^{ikx} \sum_K e^{iKx} C_{k+K} = e^{ikx} u_k(x) \ ,$$

where

$$u_k(x + na) = u_k(x) \ ,$$

is a periodic function of x with the lattice periodicity. This important result is called Bloch's Theorem.

Band structure

The eigenvalue equation

$$\left[\frac{1}{2}(k + K)^2 - E\right] C_{k+K} + \sum_{K'} V_{K-K'} C_{k+K'} = 0 \ .$$

for a given first Brillouin zone wave vector k can be solved as a matrix eigenvalue equation given the Fourier coefficients V_K of the periodic potential. The matrix involved is actually infinite dimensional, so approximations may have to be made to solve it in practice. There will be a discrete spectrum of states for each value of k. Consider any one of this spectrum of states as a function of k as it varies over the first Brillouin zone: this set of states is called a band. Thus the spectrum of the system consists of an infinite number of bands.

The reciprocal space equation above allows one approach to finding the band structure of a crystalline solid.

Another approach is to use the Bloch theorem decompostion

$$\psi_k(x) = e^{ikx} u_k(x) \ ,$$

and solve Schroedinger's equation in position space by direct integration of the differential equation in a single unit cell of the lattice, say in the interval $0 \leq x < a$. This is sufficient since $u_k(x)$ is periodic! To solve Schroedinger's differential equation we need of course to apply boundary conditions. These are also determined by Bloch's theorem

$$u_k(a) = e^{-ika} u_k(0) \ .$$

Augmented Plane Wave Method for Copper

Electronic band structure methods can be classified in two main types:

Semi-empirical Methods: These methods use an approximate phenomenological potential function in to solve for the Bloch functions of the electrons. An important example is the Augmented Plane Wave (APW) method developed by Slater Phys. Rev. 51, 846-851 (1937) and used by Burdick Phys. Rev. 129, 138-150 (1963).

Ab Initio Methods: These methods use the SCF (Hartree-Fock) or DFT to determine the Bloch functions from the Coulomb forces between the electrons and ions. For example, Car and Parinello Phys. Rev. Lett. 55, 2471-2474 (1985) used DFT combined with MD to compute the band structure of Silicon, following an earlier DFT calculation by Yin and Cohen Phys. Rev. B 26, 3259-3272 (1982).

Muffin Tin Approximation

This approximation was introduced by Slater and others to simplify the problem of solving a Schroedinger equation for the Bloch functions inside the ionic cores, now known as the Muffin Tin approximation.

The basic idea is to divide the volume into two types of regions

- Core regions with a deep attractive potential function that is spherically symmetric about the atomic center to a good approximation, and

- Interstitial regions where the potential is slowly varying with the actual symmetry of the lattice (FCC for Cu) and the wavefunctions can be approximated by a linear superpostion of plane waves.

Augmented Plane Wave (APW) Basis Functions

In the simple Kronig-Penney model, the band structure was determined by expressing the energy eigenfunction as a linear superposition of plane waves with the wavenumbers given by the reciprocal lattice vectors $\mathbf{K}$, and then diagonalizing the Hamiltonian. For the 1-D model the Hamiltonian is reduces to a a 2×2 matrix whose eigenvalues determine the dispersion function $E(k)$.

A similar procedure determines $E(\mathbf{k})$ for 3-D problems like Copper. In the muffin-tin approximation, the potential is taken to be constant in the interstitial regions and the wavefunction is taken to be a linear superposition of plane wave Bloch functions $\exp(i\mathbf{q}\cdot\mathbf{x})$ with $\mathbf{q}=\mathbf{K}+\mathbf{k}$ where $\mathbf{K}$ are reciprocal lattice vectors for the FCC lattice in the case of Copper.

Consider one of the core regions and use spherical polar coordinates $\mathbf{r}$ with origin at the center of the Cu ion core. An eigenfunction with given energy E is expanded in spherical harmonics

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l}A_{lm}\mathcal{R}_l(r)Y_{lm}(\theta,\phi)$$

where $\mathcal{R}_l(r)$ is a solution of a radial Schroedinger equation

$$-\frac{1}{2r^2}\frac{d}{dr}\left[r^2\frac{d\mathcal{R}_l}{dr}\right]+\left[\frac{l(l+1)}{2r^2}+V(r)\right]\mathcal{R}_l(r)=E\mathcal{R}_l(r)\;,$$

where $V(r)$ is a phenomenologically determined effective potential energy of motion of the valence electron inside the ionic core.

The wavefunction must be continuous at the interfaces between the core and interstitial regions. The matching condition can be derived by expanding

$$\exp(i\mathbf{q} \cdot \mathbf{r}) = 4\pi \sum_{lm} i^l j_l(qr) Y_{lm}^*(\theta_{\mathbf{q}}, \phi_{\mathbf{q}}) Y_{lm}(\theta, \phi)$$

which results in an approximate APW basis function

$$\psi_{\mathbf{q}}^{\mathrm{APW}}(\mathbf{r}) = 4\pi \sum_{lm} i^l \left[\frac{j_l(qr)}{\mathcal{R}_l(r)} \right] Y_{lm}^*(\theta_{\mathbf{q}}, \phi_{\mathbf{q}}) Y_{lm}(\theta, \phi) \ .$$

These functions are not energy eigenfunctions because their derivatives are not continuous at the core-interstitial boundaries. Also, the infinite sum over the angular momentum quantum number l must be truncated at a reasonably small finite l_{max} in a numerical calculation.

The APW functions are used as a finite basis to express the electronic wavefunction

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} C_{\mathbf{K}} \psi_{\mathbf{k}+\mathbf{K}}^{\mathrm{APW}}(\mathbf{r}) \ .$$

The coefficients $C_{\mathbf{K}}$ are determined by the lowest energy solution of a generalized eigenvalue equation

$$\mathbf{HC} = E\mathbf{SC} \ .$$

Lecture