Chapter 4

The Variational Method

The exact analytical solution of the Schrödinger equation is possible only in a few cases. Even the direct numerical solution by integration is often not feasible in practise, especially in systems with more than one particle. There are however extremely useful approximated methods that can in many cases reduce the complete problem to a much simpler one. In the following we will consider the *variational principle* and its consequences. This constitutes, together with suitable approximations for the electron-electron interactions, the basis for most practical approaches to the solution of the Schrödinger equation in condensed-matter physics.

4.1   Variational Principle

Let us consider a Hamiltonian H and a function ψ, that can be varied at will with the sole condition that it stays normalized. One can calculate the expectation value of the energy for such function (in general, not an eigenfunction of H):

$$\langle H \rangle = \int \psi^* H \psi \, dv \tag{4.1}$$

where v represents all the integration coordinates.

The *variational principle* states that functions ψ for which $\langle H \rangle$ is *stationary*—i.e. does not vary to first order in small variations of ψ—are the eigenfunctions of the energy. In other words, the Schrödinger equation is equivalent to a stationarity condition.

4.1.1   Demonstration of the variational principle

Since an arbitrary variation $\delta\psi$ of a wave function in general destroys its normalization, it is convenient to use a more general definition of expectation value, valid also for non-normalized functions:

$$\langle H \rangle = \frac{\int \psi^* H \psi \, dv}{\int \psi^* \psi \, dv} \tag{4.2}$$

By modifying ψ as $\psi + \delta\psi$, the expectation value becomes

$$
\begin{aligned}
\langle H \rangle + \delta\langle H \rangle &= \frac{\int (\psi^* + \delta\psi^*) H (\psi + \delta\psi)\, dv}{\int (\psi^* + \delta\psi^*)(\psi + \delta\psi)\, dv} \\
&= \frac{\int \psi^* H \psi\, dv + \int \delta\psi^* H \psi\, dv + \int \psi^* H \delta\psi\, dv}{\int \psi^*\psi\, dv + \int \delta\psi^*\psi\, dv + \int \psi^*\delta\psi\, dv} \\
&= \left(\int \psi^* H \psi\, dv + \int \delta\psi^* H \psi\, dv + \int \psi^* H \delta\psi\, dv \right) \times \\
&\quad \frac{1}{\int \psi^*\psi\, dv} \left(1 - \frac{\int \delta\psi^*\psi\, dv}{\int \psi^*\psi\, dv} - \frac{\int \psi^*\delta\psi\, dv}{\int \psi^*\psi\, dv} \right) \quad (4.3)
\end{aligned}
$$

where second-order terms in $\delta\psi$ have been omitted and we used the approximation $1/(1+x) \simeq 1 - x$, valid for $x << 1$. By omitting again higher-order terms:

$$
\delta\langle H \rangle = \frac{\int \delta\psi^* H \psi\, dv}{\int \psi^*\psi\, dv} + \frac{\int \psi^* H \delta\psi^*\, dv}{\int \psi^*\psi\, dv} - \langle H \rangle \left(\frac{\int \delta\psi^*\psi\, dv}{\int \psi^*\psi\, dv} + \frac{\int \psi^*\delta\psi\, dv}{\int \psi^*\psi\, dv} \right). \quad (4.4)
$$

The two terms in parentheses are complex conjugates; the same holds for the first two terms, because H is a hermitian operator, satisfying

$$
\int a^* H b\, dv = \left(\int b^* H a\, dv \right)^* \quad (4.5)
$$

for any pair of functions a and b. We can thus simplify the above expression as

$$
\delta\langle H \rangle = \left(\frac{\int \delta\psi^* H \psi\, dv}{\int \psi^*\psi\, dv} + \text{c.c.} \right) - \langle H \rangle \left(\frac{\int \delta\psi^*\psi\, dv}{\int \psi^*\psi\, dv} + \text{c.c.} \right). \quad (4.6)
$$

Let us now assume that ψ is such that $\langle H \rangle$ is stationary with respect to any variation of it: then $\delta\langle H \rangle = 0$, i.e.

$$
\int \delta\psi^* \left[H - \langle H \rangle \right] \psi\, dv + \text{c.c.} = 0 \quad (4.7)
$$

for an arbitrary variation $\delta\psi$. This implies

$$
\left[H - \langle H \rangle \right] \psi = 0 \quad (4.8)
$$

that is, ψ is a solution of the Schrödinger equation:

$$
H\psi = E\psi \quad (4.9)
$$

4.1.2 Alternative demonstration of the variational principle

A different and more general way to demonstrate the variational principle, which will be useful later, is based upon Lagrange multipliers method. This method deals with the problem of finding stationarity conditions for an integral I_0 while keeping at the same time constant other integrals $I_1 \dots I_k$. One can solve instead the equivalent problem

$$
\delta \left(I_0 + \sum_k \lambda_k I_k \right) = 0 \quad (4.10)
$$

where λ_k are constants to be determined (*Lagrange multipliers*). In our case we have

$$I_0 \ = \ \int \psi^* H \psi \, dv \tag{4.11}$$

$$I_1 \ = \ \int \psi^* \psi \, dv \tag{4.12}$$

and thus we assume

$$\delta(I_0 + \lambda I_1) = 0 \tag{4.13}$$

where λ must be determined. By proceeding like in the previous section, we find

$$\delta I_0 \ = \ \int \delta\psi^* H \psi \, dv + \text{c.c.} \tag{4.14}$$

$$\delta I_1 \ = \ \int \delta\psi^* \psi \, dv + \text{c.c.} \tag{4.15}$$

and thus the condition to be satisfied is

$$\delta(I_0 + \lambda I_1) = \int \delta\psi^*[H + \lambda]\psi \, dv + \text{c.c.} = 0 \tag{4.16}$$

that is

$$H\psi = -\lambda\psi \tag{4.17}$$

i.e. the Lagrange multiplier equals, apart from the sign, the energy eigenvalue. Again we see that states whose expectation energy is stationary with respect to any variation in the wave function are the solutions of the Schrödinger equation.

4.1.3 Ground state energy

Let us consider the eigenfunctions ψ_n of a Hamiltonian H, with associated eigenvalues (energies) E_n:

$$H\psi_n = E_n\psi_n \tag{4.18}$$

Let us label the ground state with $n = 0$ and the ground-state energy as E_0. Let us demonstrate that for any different function ψ, we have necessarily

$$\langle H \rangle = \frac{\int \psi^* H \psi \, dv}{\int \psi^* \psi \, dv} \geq E_0 \tag{4.19}$$

In order to demonstrate it, let us expand ψ using as basis energy eigenfunctions (this is always possible because energy eigenfunctions are a complete orthonormal set):

$$\psi = \sum_n c_n \psi_n \tag{4.20}$$

Then one finds

$$\langle H \rangle = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} = E_0 + \frac{\sum_n |c_n|^2 (E_n - E_0)}{\sum_n |c_n|^2} \tag{4.21}$$

This demonstrates Eq.(4.19), since the second term is either positive or zero, as $E_n \geq E_0$ by definition of ground state,

This simple result is extremely important: it tells us that any function ψ, yields for the expectation energy an upper estimate of the energy of the ground state. If the ground state is unknown, an approximation to the ground state can be found by varying ψ inside a given set of functions and looking for the function that minimizes $\langle H \rangle$. This is the essence of the variational method.

4.1.4 Variational method in practice

One identifies a set of *trial* wave functions $\psi(v; \alpha_1, \ldots, \alpha_r)$, where v are the variables of the problem (coordinates etc), $\alpha_i, i = 1, \ldots, r$ are parameters. The energy eigenvalue will be a function of the parameters:

$$E(\alpha_1, \ldots, \alpha_r) = \int \psi^* H \psi \, dv \tag{4.22}$$

The variational method consists in looking for the minimum of E with respect to a variation of the parameters, that is, by imposing

$$\frac{\partial E}{\partial \alpha_1} = \ldots = \frac{\partial E}{\partial \alpha_r} = 0 \tag{4.23}$$

The function ψ satisfying these conditions with the lowest E is the function that better approximates the ground state, among the considered set of trial functions.

It is clear that a suitable choice of the trial functions plays a crucial role and must be carefully done.

4.2 Secular problem

The variational method can be reduced to an algebraic problem by expanding the wave function into a *finite* basis of functions, and applying the variational principle to find the optimal coefficients of the development. Based on Eq. (4.10), this means calculating the *functional* (i.e. a "function" of a function):

$$
\begin{aligned}
G[\psi] &= \langle \psi | H | \psi \rangle - \epsilon \langle \psi | \psi \rangle \\
&= \int \psi^* H \psi \, dv - \epsilon \int \psi^* \psi \, dv
\end{aligned}
\tag{4.24}
$$

and imposing the minimum condition on $G[\psi]$. Such procedure produces an equation for the expansion coefficients that we are going to determine.

It is important to notice that our basis is formed by a *finite* number N of functions, and thus cannot be a complete system: in general, it is not possible to write any function ψ (including exact solutions of the Schrödinger equation) as a linear combination of the functions in this basis set. What we are going to do is to find the ψ function that better approaches the true ground state, among all functions that can be expressed as linear combinations of the N chosen basis functions.

4.2.1 Expansion into a basis set of orthonormal functions

Let us assume to have a basis of N functions b_i, between which orthonormality relations hold:

$$\langle b_i | b_j \rangle \equiv \int b_i^* b_j \, dv = \delta_{ij} \tag{4.25}$$

Let us expand the generic ψ in such basis:

$$\psi = \sum_{i=1}^{N} c_i b_i \tag{4.26}$$

By replacing Eq.(4.26) into Eq.(4.24) one can immediately notice that the latter takes the form

$$
\begin{aligned}
G(c_1, \ldots, c_N) &= \sum_{ij} c_i^* c_j H_{ij} - \epsilon \sum_{ij} c_i^* c_j \delta_{ij} \\
&= \sum_{ij} c_i^* c_j (H_{ij} - \epsilon \delta_{ij})
\end{aligned}
\tag{4.27}
$$

where we have written

$$H_{ij} = \langle b_i | H | b_j \rangle = \int b_i^* H b_j \, dv \tag{4.28}$$

Since both H and the basis are given, H_{ij} is a perfectly known square matrix of numbers. The hermiticity of the Hamiltonian operator implies that such matrix is hermitian:

$$H_{ji} = H_{ij}^* \tag{4.29}$$

(i.e. symmetric if all elements are real). According to the variational method, let us minimize Eq. (4.27) with respect to the coefficients:

$$\frac{\partial G}{\partial c_i} = 0 \tag{4.30}$$

This produces the condition

$$\sum_j (H_{ij} - \epsilon \delta_{ij}) c_j = 0 \tag{4.31}$$

If the derivative with respect to complex quantities bother you: separate the coefficients into a real and an imaginary part $c_k = x_k + i y_k$, require that derivatives with respect to both x_k and y_k are zero, find (exploiting hermiticity) a system

$$
\begin{aligned}
W_k + W_k^* &= 0 \\
-i W_k + i W_k^* &= 0
\end{aligned}
$$

where $W_k = \sum_j (H_{kj} - \epsilon \delta_{kj}) c_j$, that allows as only solution $W_k = 0$.

We note that, if the basis were a complete (and thus infinite) system, this would be the form of the Schrödinger equation. We have finally demonstrated

that the same equation, for a finite basis set, yield the best approximation to the true solution according to the variational principle.

Eq.(4.31) is a system of N algebraic linear equations, homogeneous (there are no constant term) in the N unknown c_j. In general, this system has only the trivial and unphysical solution $c_j = 0$ for all coefficients (i.e. zero wave function!). A nonzero solution exists if and only if the following condition on the determinant is fulfilled:

$$\det |H_{ij} - \epsilon \delta_{ij}| = 0 \tag{4.32}$$

Such condition implies that one of the equations is a linear combination of the others and the system has in reality $N - 1$ equations and N unknowns, thus admitting a no zero solution.

Eq.(4.32) is known as *secular equation*. It is an algebraic equation of degree N in ϵ (as it is evident from the definition of the determinant, with the main diagonal generates a term ϵ^N, all other diagonals generating lower-order terms), that admits N solutions, or eigenvalues. Eq.(4.31) can also be written in matrix form

$$H\mathbf{c} = \epsilon\mathbf{c} \tag{4.33}$$

where H is here the $N \times N$ matrix whose matrix elements are H_{ij}, $\mathbf{c}$ is the vector formed with c_i components. The solutions $\mathbf{c}$ are also called *eigenvectors*. For each root (eigenvalue) there will be a corresponding eigenvector (known within a multiplicative constant, fixed by the normalization). We have thus N eigenvectors and we can write that there are N solutions:

$$\psi_k = \sum_i C_{ik} b_i \quad , \quad k = 1, \ldots, N \tag{4.34}$$

where C_{ik} is a matrix formed by the N eigenvectors (written as columns and disposed side by side):

$$H\psi_k = \epsilon_k \psi_k \tag{4.35}$$

that is, in matrix form, taking the $i-$th component,

$$(H\psi_k)_i = \sum_j H_{ij} C_{jk} = \epsilon_k C_{ik} \tag{4.36}$$

Eq.(4.33) is a common equation in linear algebra and there are standard methods to solve it. Given a matrix H, it is possible to obtain, using standard library routines, the C matrix and a vector ϵ of eigenvalues.

The solution process is usually known as *diagonalization*. This name comes from the following important property of C. Eq.(4.34) can be seen as a *transformation* of the N starting functions into another set of N functions, via a transformation matrix. It is possible to show that if the b_i functions are orthonormal, the ψ_k functions are orthonormal as well. Then the transformation is *unitary*, i.e.

$$\sum_i C_{ij}^* C_{ik} = \delta_{jk} \tag{4.37}$$

or, in matrix notations,

$$(C^{-1})_{ij} = C_{ji}^* \equiv C_{ij}^\dagger \tag{4.38}$$

that is, the inverse matrix is equal to the conjugate of the transpose matrix, known as *adjoint* matrix. The matrix C having such property is also called a *unitary* matrix.

Let us consider now the matrix product $C^{-1}HC$ and let us calculate its elements:

$$
\begin{aligned}
(C^{-1}HC)_{kn} &= \sum_{ij}(C^{-1})_{ki}H_{ij}C_{jn} \\
&= \sum_i C_{ik}^* \sum_j H_{ij}C_{jn} \\
&= \sum_i C_{ik}^* \epsilon_n C_{in} \\
&= \epsilon_n \sum_i C_{ik}^* C_{in} \\
&= \epsilon_n \delta_{kn} \qquad\qquad (4.39)
\end{aligned}
$$

where the preceding results have been used. The transformation C reduces H to a diagonal matrix, whose non-zero N elements are the eigenvalues. We can thus see our eigenvalue problem as the search for a transformation that brings from the original basis to a new basis in which the H operator has a diagonal form, that is, it acts on the elements of the basis by simply multiplying them by a constant (as in Schrödinger equation).

4.3   Plane-wave basis set

A good example of orthonormal basis set, and one commonly employed in physics, is the *plane-wave* basis set. This basis set is closely related to Fourier transforms and it can be easily understood if concepts from Fourier analysis are known.

A function $f(x)$ defined on the entire real axis can be always expanded into Fourier components, $\widetilde{f}(k)$:

$$
f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \widetilde{f}(k)e^{ikx}dk \qquad\qquad (4.40)
$$

$$
\widetilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)e^{-ikx}dx. \qquad\qquad (4.41)
$$

For a function defined on a finite interval $[-a/2, a/2]$, we can instead write

$$
f(x) = \frac{1}{\sqrt{a}} \sum_n \widetilde{f}(k_n)e^{ik_n x} \qquad\qquad (4.42)
$$

$$
\widetilde{f}(k_n) = \frac{1}{\sqrt{a}} \int_{-a/2}^{a/2} f(x)e^{-ik_n x}dx \qquad\qquad (4.43)
$$

where $k_n = 2\pi n/a$, $n = 0, \pm 1, \pm 2, ...$ Note that the $f(x)$ function of Eq.4.42 is by construction a periodic function, with period equal to a: $f(x+a) = f(x)$, as can be verified immediately. This implies that $f(-a/2) = f(+a/2)$ must hold (also known under the name of *periodic boundary conditions*). The expressions

reported here are immediately generalized to three or more dimensions. In the following only a simple one-dimensional case will be shown.

Let us define our plane-wave basis set $b_i(x)$ according to Eq.(4.42):

$$b_i(x) = \frac{1}{\sqrt{a}} e^{ik_i x}, \qquad k_i = \frac{2\pi}{a} i, \quad i = 0, \pm 1, \pm 2, ..., \pm N \qquad (4.44)$$

and the corresponding coefficients c_i for the wave function $\psi(x)$ as

$$c_i = \int_{-a/2}^{a/2} b_i^*(x)\psi(x)dx = \langle b_i|\psi\rangle, \qquad \psi(x) = \sum_i c_i b_i(x). \qquad (4.45)$$

This base, composed of $2N + 1$ functions, becomes a complete basis set in the limit $N \to \infty$. This is a consequence of well-known properties of Fourier series. It is also straightforward to verify that the basis is orthonormal: $S_{ij} = \langle b_i|b_j\rangle = \delta_{ij}$. The solution of the problem of a particle under a potential requires thus the diagonalization of the Hamiltonian matrix, whose matrix elements:

$$H_{ij} = \langle b_i|H|b_j\rangle = \langle b_i|\frac{p^2}{2m} + V(x)|b_j\rangle \qquad (4.46)$$

can be trivially calculated. The kinetic term is *diagonal* (i.e. it can be represented by a diagonal matrix):

$$\langle b_i|\frac{p^2}{2m}|b_j\rangle = -\frac{\hbar^2}{2m} \int_{-a/2}^{a/2} b_i^*(x)\frac{d^2 b_j}{dx^2}(x)dx = \delta_{ij}\frac{\hbar^2 k_i^2}{2m}. \qquad (4.47)$$

The potential term is nothing but the Fourier transform of the potential (apart from a multiplicative factor):

$$\langle b_i|V(x)|b_j\rangle = \frac{1}{a} \int_{-a/2}^{a/2} V(x)e^{-i(k_i-k_j)x}dx = \frac{1}{\sqrt{a}}\tilde{V}(k_i - k_j). \qquad (4.48)$$

A known property of Fourier transform ensures that the matrix elements of the potential tend to zero for large values of $k_i - k_j$. The decay rate will depend upon the spatial variation of the potential: faster for slowly varying potentials, and vice versa. Potentials and wave functions varying on a typical length scale λ have a significant Fourier transform up to $k_{max} \sim 2\pi/\lambda$. In this way we can estimate the number of plane waves needed to solve a problem.

4.4   Code: pwell

Let us consider the simple problem of a potential well with finite depth V_0:

$$V(x) = 0 \quad \text{per} \quad x < -\frac{b}{2}, x > \frac{b}{2} \qquad (4.49)$$

$$V(x) = -V_0 \quad \text{per} \quad -\frac{b}{2} \le x \le \frac{b}{2} \qquad (4.50)$$

with $V_0 > 0$, $b < a$. The matrix elements of the Hamiltonian are given by Eq.(4.47) for the kinetic part. by Eq.(4.48) for the potential. The latter can be explicitly calculated:

$$
\langle b_i | V(x) | b_j \rangle = -\frac{1}{a} \int_{-b/2}^{b/2} V_0 e^{-i(k_i - k_j)x} dx \tag{4.51}
$$

$$
= -\frac{V_0}{a} \frac{e^{-i(k_i - k_j)x}}{-i(k_i - k_j)} \Big|_{-b/2}^{b/2} V_0 \tag{4.52}
$$

$$
= \frac{V_0}{a} \frac{\sin(a(k_i - k_j)/2)}{(k_i - k_j)/2}, \qquad k_i \neq k_j. \tag{4.53}
$$

The case $k_i = k_j$ must be separately treated, yielding

$$
\widetilde{V}(0) = \frac{V_0 b}{a}. \tag{4.54}
$$

Code `pwell.f90`[1] (or `pwell.c`[2]) generates the k_i, fills the matrix H_{ij} and diagonalizes it. The code uses units in which $\hbar^2/2m = 1$ (e.g. atomic Rydberg units). Input data are: width (b) and depth (V_0) of the potential well, width of the box (a), number of plane waves ($2N + 1$). On output, the code prints the three lowest energy levels; moreover it writes to file the wave function of the ground state.

The diagonalization is performed by subroutine `dsyev.f`[3] from the linear algebra library LAPACK[4]. Moreover subroutines from the BLAS[5] library (collected here: `dgemm.f`[6]) are needed.

`dsyev` uses a well-established diagonalization algorithm (reduction to tridiagonal form), valid for any $N \times N$ symmetric matrix, that requires $\mathcal{O}(\mathcal{N}^3)$ floating-point operations. The usage of `dsyev` requires either linking to a precompiled LAPACK and BLAS libraries, or compilation of the Fortran version and subsequent linking. Instructions on the correct way to call `dsyev` are contained in the header of the subroutine; if calling from C, remember that variables passed to Fortran routines must be C pointers. It may be necessary to add an underscore (as in `dsyev_()`) in the calling program.

4.4.1 Laboratory

- Observe how the results converge with respect to the number of plane waves, verify the form of the wave function. Verify the energy versus a known case. You may use for instance the following case: for $V_0 = 1$, $b = 2$, the exact result is $E = 0.4538$. You may (and should) also verify the limit $V_0 \to \infty$ (what are the energy levels?).

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[1] http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/F90/pwell.f90
[2] http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/C/pwell.c
[3] http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/Lapack/dysev.f
[4] http://www.netlib.org/lapack/
[5] http://www.netlib.org/blas/
[6] http://www.fisica.uniud.it/%7Egiannozz/Corsi/MQ/Software/Blas/dgemm.f

- Observe how the results converge with respect to a. Note that for values of a not so big with respect to b, the energy calculated with the variational method is *lower* than the exact value. Why is it so?

- Try to modify the code, adapting it to a potential well having a Gaussian form (whose Fourier transform can be analytically calculated: what is the Fourier transform of a Gaussian function?) For the same "width", which problem converges more quickly: the square well or the Gaussian well?

- We know that for a symmetric potential, i.e. $V(-x) = V(x)$, the solutions have a well-defined parity, alternating even and odd parity (ground state even, first excited state odd, and so on). Exploit this property to reduce the problem into two subproblems. one for even states and one for odd states. Use sine and cosine functions, obtained by suitable combinations of plane waves as above. Beware the correct normalization and the $k_n = 0$ term! Why is this convenient? What is gained in computational terms?