

The variational method

The Schroedinger equation can be recast in terms of a Variational problem, that gives a systematically improvable approximation to the ground state solution. Let us define the functional:

$$H[\Psi] = \frac{\int dX \Psi^*(X) H \Psi(X)}{\int dX \Psi^*(X) \Psi(X)} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

where X is a set of generalized coordinates (positions, momenta, spins, etc.). The variational principle states that for any $|\Psi\rangle$ the expectation of the Hamiltonian satisfies the following inequality:

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0,$$

where E_0 is the ground state energy of the system. Moreover, and most important, the equality holds iff $|\Psi\rangle = |\Psi_0\rangle$.

Notice that we have assumed that the state $|\Psi\rangle$ is not normalized. The variational principle tells us that in order to find $|\Psi_0\rangle$ we need to minimize the expectation of H . Let us consider a state $|\Psi\rangle + |\delta\Psi\rangle$, where $|\delta\Psi\rangle$ is some linear combination of eigenstates with coefficients $\ll 1$. Defining:

$$P = \langle\Psi|H|\Psi\rangle \quad Q = \langle\Psi|\Psi\rangle,$$

the variation of the expectation of the energy can be written as:

$$\delta E = \frac{(\langle\Psi| + \langle\delta\Psi|)H(|\Psi\rangle + |\delta\Psi\rangle)}{(\langle\Psi| + \langle\delta\Psi|)(|\Psi\rangle + |\delta\Psi\rangle)} - \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

We want to keep this expression to linear order in $|\delta\Psi\rangle$:

$$\delta E = \frac{\langle\Psi|H|\Psi\rangle + 2\langle\delta\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle + 2\langle\delta\Psi|\Psi\rangle} - \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{P + 2\langle\delta\Psi|H|\Psi\rangle}{Q + 2\langle\delta\Psi|\Psi\rangle} - \frac{P}{Q}$$

which yields:

$$\frac{PQ + 2Q\langle\delta\Psi|H|\Psi\rangle - P(Q + 2\langle\delta\Psi|\Psi\rangle)}{Q(Q + 2\langle\delta\Psi|\Psi\rangle)} = \frac{2\langle\delta\Psi|H|\Psi\rangle - P/Q}{Q}.$$

In the last step we neglect the term in $\langle\delta\Psi|\Psi\rangle$ in the denominator, since the numerator misses the order 1 terms. Since $P/Q = E[\Psi]$, we have the final expression:

$$\delta E = \frac{2\langle\delta\Psi|(H|\Psi\rangle - E[\Psi]|\Psi\rangle)}{Q}$$

In order to find the minimum of $E[\Psi]$ we want δE be 0 $\forall |\delta\Psi\rangle$. This happens iff $|\Psi\rangle = |\Psi_0\rangle$. In principle, if the states are confined in a given subspace of the Hilbert space, this expression holds for any state that gives a minimum of the energy in that given subspace.

Expansion on a basis

How can we solve the Schroedinger equation using the variational property? If we are able to find the state $|\Psi_0\rangle$ corresponding to the **absolute minimum** of the expectation of the Hamiltonian over the **whole Hilbert space** then we have the exact solution. This is a problem that is in general impossible to solve.

The usual strategy to find an *approximate* solution is that of considering a finite subset of a complete orthonormal basis $|\chi_p\rangle$, such that $\langle\chi_p|\chi_q\rangle = \delta_{pq}$.

A generic state $|\Psi\rangle$ will then be written as:

$$|\Psi\rangle = \sum_p c_p |\chi_p\rangle.$$

The energy functional becomes:

$$E[\Psi] = \frac{\sum_{p,q} c_p^* c_q H_{pq}}{\sum_{p,q} c_p^* c_q \delta_{pq}},$$

where $H_{pq} = \langle\chi_p|H|\chi_q\rangle$.

The solution of the problem is obtained by varying the energy with respect to the coefficients, and imposing that the derivative is zero. There is a very important point to keep in mind: **We need to preserve the normalization of the state we are varying!** This means that we have to request that

$$\langle \Psi | \Psi \rangle = \sum_{p,q} c_p^* c_q \delta_{pq} = 1$$

for any value of the coefficients.

We choose to vary with respect to c_p^* . The variational equation becomes then:

$$\begin{aligned} & \frac{\partial}{\partial c_p^*} \{ E[\Psi] - \epsilon_p \langle \Psi | \Psi \rangle \} = \\ & = \frac{\partial}{\partial c_p^*} \left\{ \sum_{p,q} c_p^* c_q H_{pq} - \epsilon_p \sum_{p,q} c_p^* c_q \delta_{pq} \right\} = 0 \end{aligned}$$

The previous equation corresponds to a set of M equations, where M is the number of basis states we have considered:

$$\sum_q (H_{pq} - \epsilon_p \delta_{pq}) c_q = 0 \quad p, q = 1 \dots M.$$

This is obviously an eigenvalue equation, that we might write in a compact form as:

$$\mathbf{H}\mathbf{C} = \epsilon\mathbf{C}.$$

As previously seen, \mathbf{H} is the matrix obtained computing all the matrix elements of the Hamiltonian H between the basis states. \mathbf{C} is the vector of the coefficients of the expansion over the states $|\chi_p\rangle$ that gives the eigenfunction corresponding to the eigenvalue ϵ . In general we are interested in finding the ground state eigenvalue ϵ_0 with the corresponding eigenvector, but in principle this works also for excited states.

Non-orthogonal basis sets

The simple equations we derived above are valid only if we are working with an *orthonormal* basis set. While in some cases this is easily doable, It might become cumbersome when the basis has to be built from some functions that are NOT orthonormal in origin. One of the better known examples is the Gaussian basis set, that is widely used in quantum chemistry, solid state or nuclear physics.

We will come back to Gaussians later. For now, let us just write down the variational equation in this case:

$$\sum_q (H_{pq} - \epsilon_p S_{pq}) c_q = 0 \quad p, q = 1 \dots M.$$

We have substituted the δ_{pq} (the orthonormality condition) with the so-called *overlap matrix* $S_{pq} = \langle \chi_p | \chi_q \rangle$. This equation can be written in the compact form:

$$\mathbf{HC} = \epsilon \mathbf{SC} \Rightarrow \mathbf{S}^{-1} \mathbf{HC} = \epsilon \mathbf{C}$$

which is a **generalized eigenvalue equation**.

There are several strategies to solve the generalized eigenvalue problem. A simple one consists of finding a matrix \mathbf{V} such that:

$$\mathbf{V}^T \mathbf{S} \mathbf{V} = \mathbb{I}.$$

This can be achieved by diagonalizing \mathbf{S} and then defining as \mathbf{U} the orthogonal matrix made up by its eigenvectors. Calling $\mathbf{\Lambda}$ the matrix of the eigenvalues of \mathbf{S} we have:

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{\Lambda}.$$

Since the eigenvalues λ_i of \mathbf{S} will all be positive, we can define the matrix $\mathbf{S}^{-\frac{1}{2}}$ by taking the diagonal matrix made by the elements $\lambda_i^{-\frac{1}{2}}$. At this point we can define the (non-orthogonal!) matrix:

$$\mathbf{V} = \mathbf{U} \mathbf{S}^{-\frac{1}{2}}.$$

In fact:

$$\mathbf{V}^T \mathbf{S} \mathbf{V} = \mathbf{S}^{-\frac{1}{2}} \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \mathbf{S}^{-\frac{1}{2}} = \mathbb{I}.$$

Now we can define a transformed Hamiltonian matrix $\mathbf{H}' = \mathbf{V}^T \mathbf{H} \mathbf{V}$. Then, let us diagonalize \mathbf{H}' :

$$\mathbf{H}' \mathbf{C}' = \mathbf{E} \mathbf{C}'$$

where \mathbf{E} is the (diagonal) matrix of the eigenvalues of \mathbf{H}' . Since the eigenvectors matrix \mathbf{C}' is orthogonal, we can write:

$$\mathbf{C}'^\dagger \mathbf{H}' \mathbf{C}' = \mathbf{E} \Rightarrow \mathbf{C}'^\dagger \mathbf{V}^T \mathbf{H} \mathbf{V} \mathbf{C}' = \mathbf{E}.$$

Multiplying the r.h.s. from the left by $\mathbf{C}'^\dagger \mathbf{C}'$ and then inserting $\mathbf{V}^T \mathbf{S} \mathbf{V}$, both identities, we obtain:

$$\mathbf{C}'^\dagger \mathbf{V}^T \mathbf{H} \mathbf{V} \mathbf{C}' = \mathbf{C}'^\dagger \mathbf{V}^T \mathbf{S} \mathbf{V} \mathbf{C}' \mathbf{E},$$

Implying:

$$\mathbf{H} \mathbf{V} \mathbf{C}' = \mathbf{E} \mathbf{S} \mathbf{V} \mathbf{C}',$$

since $(\mathbf{C}'^\dagger \mathbf{V}^T)^{-1}$ exists (prove it). This proves that the eigenvalues of \mathbf{H}' and the vectors $\mathbf{V} \mathbf{C}'$ are the eigenvalues and eigenvectors, respectively, of the generalized eigenvalue problem.

The algorithm then goes as follows:

1. Compute and diagonalize the overlap matrix $S_{pq} = \langle \chi_p | \chi_q \rangle$, finding the eigenvectors matrix \mathbf{U} (in gsl routines this is directly given as output), and the eigenvalues.
2. Build the matrix $\mathbf{V} = \mathbf{S}^{-\frac{1}{2}} \mathbf{U}$ (this is not a true matrix product, you just need to multiply each row of \mathbf{U} by the inverse of the square root of the eigenvalue of \mathbf{S} with the same index).
3. Compute the transformed Hamiltonian $\mathbf{H}' = \mathbf{V}^T \mathbf{H} \mathbf{V}$, and diagonalize it, finding the eigenvalues \mathbf{E} and the eigenvectors \mathbf{C}' .
4. Compute the eigenvectors of the general eigenvalue problem by the product $\mathbf{C} = \mathbf{V} \mathbf{C}'$.

Note:

- ▶ Diagonalizations, transpositions, matrix products should be performed preferentially by library routines.
- ▶ Library routines exist for directly solving the GE problem

One dimensional square well

WARM UP PROBLEM: Find the ground state and the first three excited states of the potential well defined by the potential:

$$V(x) = \begin{cases} \infty & \text{for } |x| > 1 \\ 0 & \text{for } |x| < 1 \end{cases}$$

using the basis functions:

$$\chi_n(x) = \begin{cases} x^n(1+x)(1-x) & \text{for } |x| < 1 \\ 0 & \text{for } |x| > 1 \end{cases} \quad n = 0, 1 \dots M.$$

Study the convergence of the levels as a function of M . Assume $\hbar^2/2m = 1$.

Some help:

- The overlap matrix is:

$$S_{nm} = \langle \chi_n | \chi_m \rangle = \int_{-1}^1 \chi_n(x) \chi_m(x) dx =$$
$$= \begin{cases} \frac{2}{n+m+5} - \frac{4}{n+m+3} + \frac{2}{n+m+1} & \text{for } n+m \text{ even} \\ 0 & \text{for } n+m \text{ odd} \end{cases}$$

- The Hamiltonian matrix (kinetic energy only!) is:

$$H_{nm} = \langle \chi_n | p^2 | \chi_m \rangle = - \int_{-1}^1 \chi_n(x) \frac{d^2}{dx^2} \chi_m(x) dx =$$
$$= \begin{cases} -8 \frac{1-m-n-2mn}{(m+n+3)(m+n+1)(m+n-1)} & \text{for } n+m \text{ even} \\ 0 & \text{for } n+m \text{ odd} \end{cases}$$