function of the system. This selection is based on physical grounds and past experience, and depends on the system. Since the set is finite, the function obtained will be approximate; nevertheless, it is customary to call it a basis set. Here we will discuss the method for obtaining the best (i.e. minimizing the energy) combination coefficients.

The basis set is $\{u_i, i = 1, \cdots, N\}$. It is not assumed to be orthogonal, because in many cases it is convenient to use nonorthogonal sets. The function is expanded in the basis

$$\phi = \sum_{i=1}^{N} c_i u_i$$

$$E' = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\sum_{j=1}^{N}\sum_{i=1}^{N} c_j^* c_i H_{ji}}{\sum_{j=1}^{N}\sum_{i=1}^{N} c_j^* c_i S_{ji}},$$

where $H_{ji} \equiv \langle u_j|H|u_i\rangle, \quad S_{ji} \equiv \langle u_j|u_i\rangle$.

Note that H_{ji} and S_{ji} are constant numbers, although the integrals may in some cases be rather difficult to calculate.

The equations above may be written as

$$\sum_{j=1}^{N}\sum_{i=1}^{N} c_j^* c_i \left(H_{ji} - E' S_{ji}\right) = 0.$$

Since we are looking for a minimum of E', $\partial E'/\partial c_i = 0$. The total differential of the equation is therefore

$$\sum_{j=1}^{N} dc_j^* \sum_{i=1}^{N} c_i(H_{ji} - E' S_{ji}) + \sum_{i=1}^{N} dc_i \sum_{j=1}^{N} c_j^*(H_{ji} - E' S_{ji}) = 0.$$

We can always change summation indices, as long as we do it consistently. In the first sum we will replace i by j and j by i, giving

$$\sum_{i=1}^{N} dc_i^* \sum_{j=1}^{N} c_j (H_{ij} - E' S_{ij}) + \sum_{i=1}^{N} dc_i \sum_{j=1}^{N} c_j^* (H_{ji} - E' S_{ji}) = 0.$$

This equation holds for any choice of the differentials $\{dc_i\}$. We choose all $dc_i = 0$, except one $dc_k = a$. For this choice

$$a^* \sum_{j=1}^{N} c_j (H_{kj} - E' S_{kj}) + a \sum_{j=1}^{N} c_j^* (H_{jk} - E' S_{jk}) = 0.$$

Now choose all $dc_i = 0$, except $dc_k = \imath a$ (this $\imath$ is $\sqrt{-1}$), giving

$$-\imath a^* \sum_{j=1}^{N} c_j (H_{kj} - E' S_{kj}) + \imath a \sum_{j=1}^{N} c_j^* (H_{jk} - E' S_{jk}) = 0.$$

The last two equations give

$$\sum_{j=1}^{N} c_j (H_{kj} - E' S_{kj}) = 0 \quad \text{and} \quad \sum_{j=1}^{N} c_j^* (H_{jk} - E' S_{jk}) = 0.$$

The second equation is just the Hermitian conjugate of the first. Again we get secular equations, which have non-trivial solutions only if the determinant $|H_{ji} - E' S_{ji}| = 0$.

The secular determinant is zero for N values of E', which may be ordered

$$E'_1 \leq E'_2 \leq \cdots \leq E'_N.$$

The lowest energy obtained this way is an upper bound to the lowest eigenvalue of the Hamiltonian,

$$E'_1 \geq E_1.$$

It can be shown that the other E'_n provide bounds to respective eigenvalues,

$$E'_n \geq E_n.$$

If we substitute in the secular equations one of the values E'_n for which the secular determinant vanishes, the N equations

$$\sum_{j=1}^{N}(H_{ij} - E'_n S_{ij})c_j^{(n)} = 0, \quad i = 1, \cdots, N$$

become linearly dependent. They will therefore have a non-trivial solution, which may be obtained in principle by solving $N-1$ equations and expressing $N-1$ coefficients $c_j^{(n)}$ in terms of one coefficient, say $c_1^{(n)}$. This coefficient may be found by normalizing the total function. If the H_{ji} integrals are collected in a matrix $\mathbf{H}$, S_{ji} in $\mathbf{S}$, and $c_j^{(n)}$ in the column vector $\mathbf{c^{(n)}}$, the secular equations are written as

$$(\mathbf{H} - E'_n\mathbf{S})\mathbf{c^{(n)}} = 0.$$

The matrix $\mathbf{H}$ represents the operator $\hat{H}$ in the N-dimensional space spanned by the $\{u_i\}$ basis. This space is finite and not complete, and the energies and wave functions are therefore approximate. As $N \to \infty$, the representation becomes exact.

The solution of these equations is similar to matrix diagonalization (it is exactly matrix diagonalization if the basis is orthonormal, making $\mathbf{S}$ a unit matrix). Solving the equations will yield all eigenvalues and eigenfunctions.

In practice, very large basis sets (many millions) can be used. It is not possible to find all the eigenvalues and eigenfunctions in such cases, and we are not interested in all of them. Highly efficient algorithms have been devised to find a few lowest energies and corresponding functions.

Example: Particle in a box.

$$V = \begin{cases} 0 & 0 \leq x \leq l \\ \infty & \text{elsewhere} \end{cases}$$

Find approximate energies of 4 lowest levels.

The system is symmetric for reflection about $x = \frac{1}{2}l$. The wavefunction must therefore be odd or even with respect to the reflection, and the odd and even levels can be treated separately, as the H and S integrals between odd and even levels vanish.

The trial functions:
Even: $f_1 = x(l-x)$, $\quad f_2 = x^2(l-x)^2$
Odd: $f_3 = x(l-x)(\frac{1}{2}l - x)$, $\quad f_4 = x^2(l-x)^2(\frac{1}{2}l - x)$.

Calculating the H_{ji} and S_{ji} integrals and substituting in the secular determinant gives for the even functions

$$\begin{vmatrix} \frac{\hbar^2 l^3}{6m} - \frac{l^5}{30}E' & \frac{\hbar^2 l^5}{30m} - \frac{l^7}{140}E' \\ \frac{\hbar^2 l^5}{30m} - \frac{l^7}{140}E' & \frac{\hbar^2 l^7}{105m} - \frac{l^9}{630}E' \end{vmatrix} = 0.$$

The first solution, approximating the ground state energy, is $E'_1 = 0.1250018\frac{h^2}{ml^2}$. The exact energy is $0.125\frac{h^2}{ml^2}$, so the approximation is only 0.0014% off. We solved this system earlier, using the function f_1 only, and got an error of 1.3%, so adding the second function reduced the error by three orders of magnitude! This is not a typical example.

The second solution approximates the third level and gives $E'_3 = 1.293495\frac{h^2}{ml^2}$. The exact energy of this state is $1.125\frac{h^2}{ml^2}$, and the error is 15.0%. For the odd levels we get the approximate energies $E'_2 = 0.5002930\frac{h^2}{ml^2}$ and $E'_4 = 2.5393425\frac{h^2}{ml^2}$. Comparison with the exact results, $0.5\frac{h^2}{ml^2}$ and $2\frac{h^2}{ml^2}$, gives errors of 0.059% and 27.0%. The results are excellent for the two low levels and poor for the next two. Adding more functions to the basis will improve the latter.

Excited states

So far we discussed upper bounds to the ground state energy. It is easily shown (exercise) that a function known to be orthogonal to the n lowest eigenfunctions of H provides an upper bound to the energy of level $n+1$. This is particularly useful for the lowest fumction of a symmetry, since we know it is orthogonal to functions with different symmetry, hence to all lower functions. The linear variation method has the additional advantage of always giving bounds to excited states. If the roots of the secular equations are ordered, $E'_1 \leq E'_2 \leq \cdots \leq E'_N$, it can be shown that $E'_i \geq E_i$, where E_i is the ith eigenvalue of H. This holds true if we look at each symmetry separately.

Here we end the general presentation of approximate methods. The rest of the course will involve applications to systems (atoms, molecules). All these systems are far too complicated for analytical solutions, and approximations must be used. However, there is information which can be stated exactly. This information is given by operators which commute with H (symmetry operators), and is used to understand and classify the energy levels of the system and to facilitate their approximate evaluation.