

# Chapter 6

## Basis Sets

### 6.1 Introduction

In previous lectures, we introduced the *variational method* as a means of finding an approximate value for the ground state energy without knowing the exact ground state wavefunction. Knowing the ground state energy, and how it varies under controlled conditions, is a very useful way of calculating many properties of a quantum system. In many cases, the best way to do this calculation is to use the linear (matrix) method, wherein the unknown wavefunction  $\psi(x)$  is expanded in terms of some basis set of known functions  $\{\chi_i(x)\}$  :

$$\psi(x) = \sum_{i=1}^N c_i \chi_i(x) \quad (6.1)$$

where the  $\{c_i\}$  are the complex expansion coefficients. Note that in general the set  $\{\chi_i(x)\}$  must be linearly independent in order to form a basis set, but they do not need to be complete, nor orthogonal, nor normalized! In this lecture we will discuss some of the most common choices of basis sets, their usage and implications. These will form some of the basic tools used in many different computational QM approaches, such as will be discussed in the remaining lectures.

### 6.2 Revision of variational method

In an earlier lecture we saw that the task of finding a variational value for the ground state energy of a system is equivalent to solving the matrix equation:

$$\mathbf{H}\mathbf{C} = E\mathbf{S}\mathbf{C} \quad (6.2)$$

where  $\mathbf{H}$  is the Hamiltonian matrix,  $\mathbf{S}$  is the overlap matrix and  $\mathbf{C}$  is the vector of expansion coefficients. Non-trivial solutions to this matrix equation

are only possible if the equation is singular, i.e. the determinant:

$$|\mathbf{H} - E\mathbf{S}| = 0 \quad (6.3)$$

which can then be solved for the eigenenergies  $\{E\}$  in the usual way.

The solution of equation 6.3 is much simpler with an appropriate choice of basis set. This should be chosen to satisfy the appropriate boundary conditions, and also to be similar in “shape” to the solution functions, so that a minimal number of basis functions are required to achieve convergence in the results. Note that if the  $\chi_i$  basis functions are orthonormal, then the overlap matrix reduces to the identity matrix and life is a bit simpler.

For example, in the example of the infinitely deep square well discussed in an earlier lecture, we used a simple polynomial basis set as it led to simple expressions for the overlap integrals. However, an equally valid (and perhaps more obvious) choice for a basis set would be the  $\{\sin(nx), \cos(nx), 1\}$  set used in Fourier series, with appropriate boundary conditions, e.g.  $\psi(x) \rightarrow 0$  at  $x = \pm\pi$ .

More useful for calculations of atoms in molecules are the atomic orbitals  $\{e^{-\xi r} Y_{l,m}(\theta, \phi)\}$  found as solutions to the Schrödinger equation for an isolated hydrogen atom. Unfortunately, these form a non-orthogonal basis, with non-trivial overlap integrals, and the more complicated *generalized eigenvalue problem* must be solved. There are two common approaches to this problem:

Chemists, whose interest is primarily molecules or small clusters of atoms, typically use Gaussian basis sets  $\{e^{-\alpha r^2}\}$ . These still form a non-orthogonal basis set, but have the advantage that many of the overlap integrals can be done analytically. The basis functions are short-ranged and have a similar “shape” to the atomic wavefunction, and an atomic orbital can typically be fitted by a few Gaussians. Consequently, a small basis set (typically 3 or 4 Gaussian functions/orbital/atom) may be used. We will discuss this approach in more detail in section 6.3.

Physicists, whose interest is primarily extended systems, prefer to exploit Bloch’s theorem and use a plane-wave basis set,  $\{e^{i\mathbf{k}\cdot\mathbf{r}}\}$ . The plane-waves form an orthogonal basis set, with the periodicity given by the unit cell, but typically require many more basis functions (typically 50-100 plane-waves/electron). One advantage of the plane-wave basis is that it is particularly trivial to Fourier transform, which makes calculations of derivatives of the energy (e.g. forces) very simple. We will discuss plane-waves and some common tricks to improve their efficiency in section 6.4.

### 6.3 Atomic-style basis functions

Perhaps the most obvious basis set to choose in any atomic calculation is that of atomic orbitals, that is, the eigenfunctions of an isolated atom. As the

atoms in a solid or molecule come together to form bonds, the inner electronic orbitals of each atom will be only slightly modified, whereas the outer ones will overlap with those on other atoms to form *hybrid* orbitals. The result is known as the Linear Combination of Atomic Orbitals (LCAO) method, and is widely used in different quantum chemistry methods. Unfortunately, analytic forms for atomic orbitals are only known for the hydrogen atom! Therefore we assume that an atomic orbital for any single atom can be written in the general form of a *Slater-type orbital* (STO):

$$\chi_\mu(\mathbf{r}, \mathbf{R}) = r^m P_l(x, y, z) e^{-\mu(\mathbf{r}-\mathbf{R})} \quad (6.4)$$

where  $r^m$  is a simple polynomial forming the radial part of the orbital and depends on the quantum number  $n$ ,  $P_l$  is the appropriate Legendre polynomial at angular momentum  $l$ ,  $\mu$  is the “range” of the orbital and  $\mathbf{R}$  is the centre-of-mass coordinate of the atom. This works very well for atoms, and optimal values for  $\mu$  can be found which minimize the energy of the atom for a given set of basis atomic orbitals.

Unfortunately, this approach does not work well when there is more than one atom present as the integrals required to evaluate the energy from the Hamiltonian often require products of two or four such exponentials, which are hard to calculate. For instance, if we assume that each electron interacts with the average charge density of the  $N - 1$  others, then we may write a simple form of the electron-electron interaction as:

$$V_{e-e} = \sum_{i=1}^N \int |\chi_i(\mathbf{r}')|^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6.5)$$

which is known as the *Hartree potential*. Using this we may then calculate the Hartree energy (part of the total energy) from integrals such as

$$\int \chi_k^*(\mathbf{r}) V_{e-e} \chi_k(\mathbf{r}) d\mathbf{r} \quad (6.6)$$

which clearly involves products of four exponentials in this case.

However, these integrals are considerably easier to calculate if we replace the exponentials by *primitive Gaussian functions*, resulting in so-called Gaussian-type orbitals (GTOs):

$$\chi_\alpha(\mathbf{r}, \mathbf{R}) = Q_M(x, y, z) e^{-\alpha(\mathbf{r}-\mathbf{R})^2} \quad (6.7)$$

where  $Q_M$  is given by the *spherical harmonics* in Cartesian form. This is because of the “Gaussian product theorem”, that is, the product of two Gaussians centred on different atoms can be expressed as a new Gaussian centred on the “centre-of-mass” of the two atoms:

$$e^{-\alpha(\mathbf{r}-\mathbf{R}_A)^2} e^{-\beta(\mathbf{r}-\mathbf{R}_B)^2} = e^{-(\alpha+\beta)(\mathbf{r}-\mathbf{R}_P)^2} \quad (6.8)$$

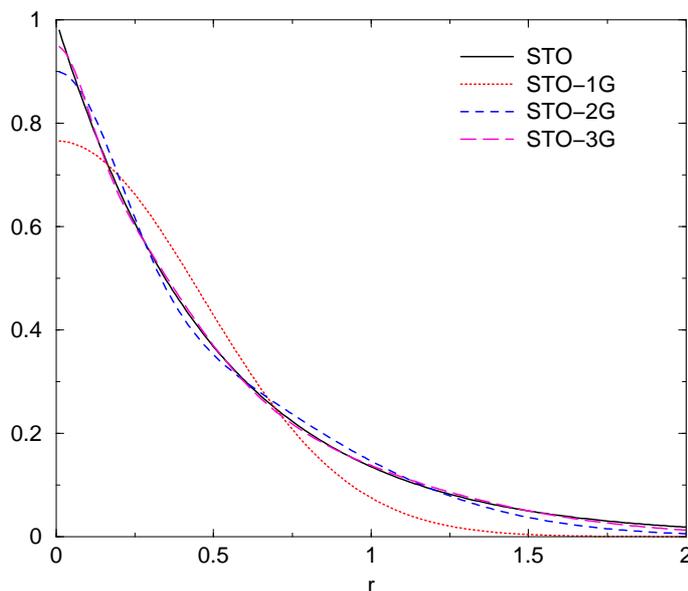


Figure 6.1: Approximation of a 1s Slater-type orbital using 1,2 and 3 Gaussians, i.e. STO-1G to STO-3G.

where

$$\mathbf{R}_P = \frac{\alpha \mathbf{R}_A + \beta \mathbf{R}_B}{\alpha + \beta} \quad (6.9)$$

which means that many of the two-electron integrals can now be done analytically.

The *minimal basis set* contains one GTO per atomic orbital. The value of  $\alpha$  in the exponent is then chosen such that the GTO fits the atomic orbital in some optimal way. This is not very satisfactory. A better approach is to have multiple GTOs per atomic orbital. The coefficients of each Gaussian may be found by fitting to the STO solution of the atomic calculation. These are then combined in fixed linear combinations to form a new basis set, which obviously has less basis functions than component GTOs, and hence is known as a *contracted basis set*. See figure 6.1 for an example of using this procedure with the simplest possible STO.

This is why the individual GTOs are called primitive functions, as they are used to build the basis functions of the contracted set. It is also possible to take an intermediate approach, and contract some but not all of the GTOs resulting in a *split-basis set*. There are many other variants upon such themes.

Obviously, when reporting the results of a quantum chemistry calculation it is important to specify the size and type of basis set used, so that some assessment of the accuracy of the calculation may be made. There is a common shorthand for this: saying that a calculation used an STO-3G basis

means that 3 GTOs have been contracted to make each STO, similarly an STO-31 basis means that 3 GTOs have been contracted and that 1 (the outermost one) has not been contracted.

Note that the use of GTOs as a basis implies that the basis functions are not orthogonal - therefore as discussed in earlier lectures on the Variational Method, the generalised eigenvalue problem will have to be solved.

### 6.3.1 Aside - Solving the generalized eigenvalue problem

In order to solve the generalized eigenvalue problem, equation 6.2, we must perform a basis transformation to convert the overlap matrix  $\mathbf{S}$  into the unit matrix  $\mathbf{I}$  which will then make it possible to convert the problem into the normal form. We start by diagonalizing the overlap matrix:

$$\mathbf{S}_{diag} = \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \quad (6.10)$$

and then noticing that the eigenvalues of  $\mathbf{S}$  are positive-definite, it is possible to define  $(\mathbf{S}_{diag})^{-\frac{1}{2}}$  (which is just the inverse of the square root of the eigenvalues of  $\mathbf{S}$  on the leading diagonal), and so

$$(\mathbf{S}_{diag})^{-\frac{1}{2}} \mathbf{U}^\dagger \mathbf{S} \mathbf{U} (\mathbf{S}_{diag})^{-\frac{1}{2}} = \mathbf{V}^\dagger \mathbf{S} \mathbf{V} = \mathbf{I} \quad (6.11)$$

which means that the matrix

$$\mathbf{V} = \mathbf{U} (\mathbf{S}_{diag})^{-\frac{1}{2}} \quad (6.12)$$

has the desired property of converting the overlap matrix into the unit matrix.

We can now substitute this into equation 6.2 as:

$$\mathbf{V}^\dagger \mathbf{H} \mathbf{V} \mathbf{V}^{-1} \mathbf{C} = \mathbf{E} \mathbf{V}^\dagger \mathbf{S} \mathbf{V} \mathbf{V}^{-1} \mathbf{C}$$

and so defining

$$\mathbf{C}' = \mathbf{V}^{-1} \mathbf{C} \quad (6.13)$$

$$\mathbf{H}' = \mathbf{V}^\dagger \mathbf{H} \mathbf{V} \quad (6.14)$$

we now obtain

$$\mathbf{H}' \mathbf{C}' = \mathbf{E} \mathbf{C}' \quad (6.15)$$

which is just the normal eigenvalue problem but with transformed matrices. We can now solve this using standard techniques to get the eigenvalues  $\{E\}$  and eigenvectors  $\mathbf{C}'$  which can then be transformed into the eigenvectors of the original problem by inverting equation 6.13.

## 6.4 Solid-style basis functions

When considering solids (or liquids) rather than isolated molecules, we are more concerned with extended (infinite) systems. Hence the most common choice of basis function in this case is the *plane-wave* and so we can expand our wavefunction as:

$$\psi(\mathbf{r}) = \sum_{\mathbf{g}} c_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{r}} \quad (6.16)$$

where  $\mathbf{g}$  is a *reciprocal lattice vector*. If we now apply *periodic boundary conditions* it can be seen that  $\{\mathbf{g}\}$  form a discretized set as there must be a longest wavelength that can be represented within the periodic unit cell, corresponding to a shortest  $\mathbf{g}$ . This plane-wave expansion, of course, is an infinite expansion in principle and so in practice must be truncated at some maximum cutoff energy, given by:

$$E_{cut} = \frac{\hbar^2 |\mathbf{g}_{max}|^2}{2m} \quad (6.17)$$

The choice of the plane-wave basis has several advantages - it is position independent (unlike atom-centred Gaussians) which makes moving the atoms around straightforward. It is also unbiased, and simple to extend - if we want to improve the basis by adding more basis functions, then this can simply be done by increasing the cutoff energy. It is also simple to *Fourier transform* the wavefunction from *real space* to *reciprocal space* (beloved of condensed matter physicists) which from a computational point of view, makes the calculation of the kinetic energy (and any other derivatives) trivial:

$$\nabla^2 \psi = \sum_{\mathbf{g}} |\mathbf{g}|^2 c_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{r}} \quad (6.18)$$

One disadvantage of plane-waves, however, is that whilst they are a natural basis for describing the smoothly varying wavefunction far from an atom, they do not closely represent the wavefunction close to the atom. For this reason, a plane-wave basis set tends to contain many more elements than the corresponding Gaussian-type orbital basis. Worst of all, is that certain wavefunctions, such as the 1s state of hydrogen, have a *cusp* at the origin (see figure 6.2), which is impossible to fit with a finite number of plane-waves. This is commonly dealt with by the *pseudo-potential approximation*.

### 6.4.1 Pseudo-potentials

When considering the electronic properties of a material, such as the making of chemical bonds, the quantity of interest is the wavefunction at some distance from the atomic centre. Indeed, with multi-electron atoms, many of the electrons play no part at all in everyday processes. This leads to a natural

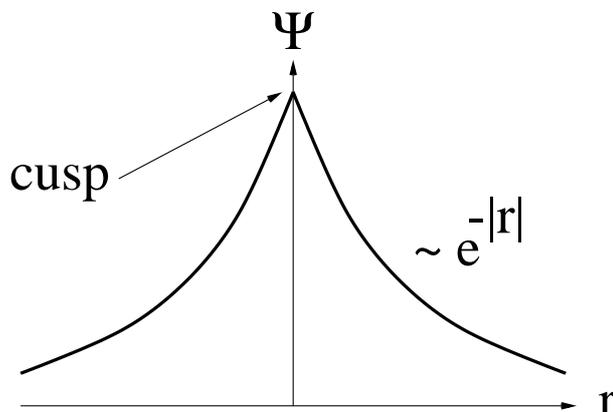


Figure 6.2: 1s hydrogenic wavefunction showing cusp at origin.

division of the electrons into *core* and *valence* electrons. The core electrons do not contribute to the properties of interest and so may be combined with the atomic nucleus to form an inert ion, whereas the valence electrons will need to be treated in detail. This reduces the number of electrons that need to be considered in the problem.

Moreover, we do not need to have an accurate wavefunction for all distances from the nucleus, but only those beyond some critical radius where the physically relevant processes take place, such as inter-atom wavefunction overlap in bond formation. Within this radius the valence wavefunction will in general have various nodes because of the requirements of orthogonality to the core wavefunctions. This means that it will be rapidly changing and again require many plane-waves to fit it accurately. However, we may (with some care) approximate the wavefunction within this region without effecting any physical observables. This is the basis of the pseudo-potential approximation - we replace the true ionic potential by a much smoother *pseudo-potential* within some critical radius, so that the corresponding *pseudo-wavefunction* is smooth and can be represented in many fewer plane-waves. There must be careful matching of the pseudo and true potentials at the critical radius, so that outside this critical radius the pseudo-wavefunction is identical to the true wavefunction. This is shown in figure 6.3. The net result is that we can correctly reproduce the original wavefunction in the physically relevant region of space with many fewer plane-waves than would otherwise be necessary.

### 6.4.2 Supercells

At this point, you may be wondering how can we have reciprocal lattice vectors if we are trying to treat a molecule - surely they only exist in infinite periodic systems? The answer is that we use the *supercell technique* - that is,

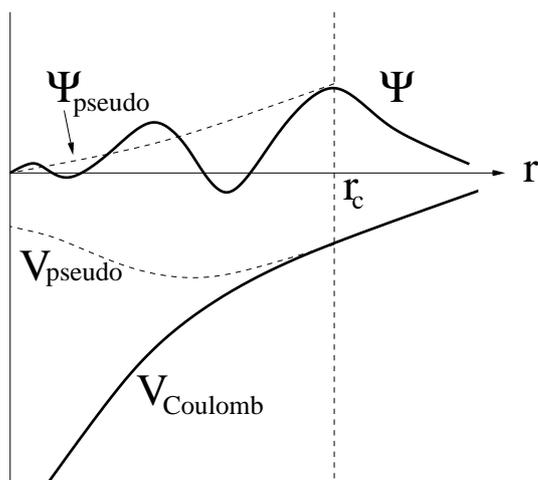


Figure 6.3: Schematic showing the original electron-ion potential and corresponding wavefunction (solid lines), and the replacement pseudo-potential and pseudo-wavefunction (dashed lines). The pseudo-potential (wavefunction) is matched onto the original potential (wavefunction) at the radius  $r_c$  and beyond this radius there is no difference.

any non-periodic structure is placed within a sufficiently large unit cell and repeated with periodic boundary conditions. Obviously, if the intention is to calculate the properties of a single isolated molecule, then the size of this cell must be chosen sufficiently large that there is negligible overlap between the wavefunction of the molecule and that of its periodic images. Using this technique of supercells, it is then possible to calculate many different kinds of systems, including molecules, clusters of atoms, surfaces, etc.

## 6.5 Final comments

A few final points to highlight:

- We can express a wavefunction in terms of basis functions, which then turns the Schrödinger equation into an eigenvalue equation which can then be solved numerically using the linear variational method.
- If the basis set is incomplete, then the eigenvalues obtained will be upper bounds on the true eigenvalues.
- If the basis set is non-orthogonal, then the generalized eigenvalue problem has to be solved.
- Within quantum chemistry, a Gaussian basis set is often used.
- Within physics, a plane-wave basis set is often used.

## 6.6 Further reading

- Basis sets in “Methods of Electronic Structure Calculations” by M. Springborg, Chapter 10
- Gaussian basis sets in “Computational Physics” by J.M. Thijssen, section 4.6

