

Chapter 5

Total Energies

5.1 Why study total energies?

For the remainder of this lecture course, we will be considering various techniques for calculating the total energy of a system of interacting quantum particles. Why is this of interest? The simple answer is that many quantities of interest can be derived from a knowledge of the total energy, or differences in total energy, and how it varies under various perturbations. In condensed matter physics, we are interested primarily in a system of electrons and ions. This is the class of system we shall consider for the rest of this lecture course.

For instance, the equilibrium lattice constant of a crystal is that which minimises the total energy. Similarly, the equilibrium bond lengths of atoms in molecules, and the structure of surfaces and defects, will all be those which minimise the total energy. For example, if a series of total energy calculations are performed as a function of the lattice parameter, then when plotted as in figure 5.1, the predicted theoretical equilibrium lattice parameter can be seen as the minimum of this curve. This can also be repeated for different crystal structures, e.g. face-centred cubic, body-centred cubic, etc. to create a family of such curves, from which the most stable crystal structure at a given applied pressure can be deduced. In this way, phase-transition pressures can be calculated. Similarly, various elastic constants of the crystal, phonon modes, piezoelectric constants, etc. can also be calculated.

Whilst such quantities can often be simply measured in a laboratory, this is not always the case. For example, there is a lot of interest in knowing the structure and elastic properties of iron at temperatures in the range 4000 K to 8000 K and pressures of 500,000 to 3,500,000 atmospheres! Why? Because this is believed to be the conditions that exist in the Earth's core and the properties of iron in such conditions are largely unknown, yet hugely important for determining the structure and dynamics of the planet! There are many other cases, where it is preferred to calculate rather than measure such quantities, for example, when designing candidate new ultra-hard materials

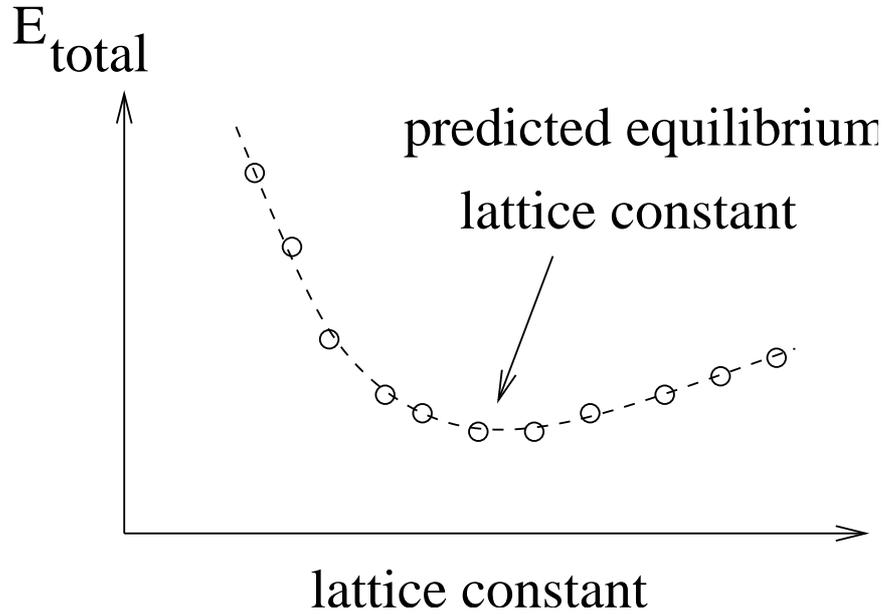


Figure 5.1: Sketch of variation in total energy with lattice constant, showing how the equilibrium value can be predicted.

to know if it is worth bothering to try to make them!

5.1.1 Forces

We can also go beyond simply calculating the total energy. For example, we know that in classical mechanics, that the force on a particle can be derived from the potential:

$$\mathbf{F} = -\nabla V(\mathbf{r}) \quad (5.1)$$

and the corresponding expression in quantum mechanics is

$$\mathbf{F} = -\nabla \langle E \rangle \quad (5.2)$$

where $\langle E \rangle$ is the expectation value of the total energy

$$\begin{aligned} \langle E \rangle &= \frac{\int \phi^*(\mathbf{r}) \hat{H} \phi(\mathbf{r}) d^3r}{\int \phi^*(\mathbf{r}) \phi(\mathbf{r}) d^3r} \\ &= N \int \phi^*(\mathbf{r}) \hat{H} \phi(\mathbf{r}) d^3r \end{aligned} \quad (5.3)$$

where $\phi(\mathbf{r})$ is the wavefunction of the system (not necessarily an eigenfunction of the Hamiltonian) and N is an appropriate normalisation constant. Therefore the force on the ions is

$$\mathbf{F} = -N \left\{ \int \nabla \phi^*(\mathbf{r}) \hat{H} \phi(\mathbf{r}) d^3r + \int \phi^*(\mathbf{r}) \nabla \hat{H} \phi(\mathbf{r}) d^3r + \int \phi^*(\mathbf{r}) \hat{H} \nabla \phi(\mathbf{r}) d^3r \right\} \quad (5.4)$$

by the chain rule.

That is, we can use the change in the expectation value of the total energy of the system upon moving the ionic coordinates $\{\mathbf{R}\}$ to derive the forces upon the ions. Note that if we expand the wavefunction of the system in some position-independent basis-set, such as plane-waves:

$$\phi(\mathbf{r}) = \sum_k c_k e^{i\mathbf{k}\cdot\mathbf{r}} \quad (5.5)$$

then we can use the *Hellmann-Feynman theorem* to rewrite equation 5.4 as

$$\begin{aligned} \mathbf{F} &= -N \nabla \left\{ \int \phi^*(\mathbf{r}) \hat{H} \phi(\mathbf{r}) d^3r \right\} \\ &= -N \nabla \left\{ \int \sum_{k'} c_{k'}^* e^{-i\mathbf{k}'\cdot\mathbf{r}} \hat{H} \sum_k c_k e^{i\mathbf{k}\cdot\mathbf{r}} d^3r \right\} \\ &= -N \nabla \left\{ \sum_{k'/k} c_{k'}^* c_k \int e^{-i\mathbf{k}'\cdot\mathbf{r}} \hat{H} e^{i\mathbf{k}\cdot\mathbf{r}} d^3r \right\} \\ &= -N \sum_{k'/k} c_{k'}^* c_k \nabla \left\{ \int e^{-i\mathbf{k}'\cdot\mathbf{r}} \hat{H} e^{i\mathbf{k}\cdot\mathbf{r}} d^3r \right\} \\ &= -N \sum_{k'/k} c_{k'}^* c_k \int e^{-i\mathbf{k}'\cdot\mathbf{r}} \nabla \hat{H} e^{i\mathbf{k}\cdot\mathbf{r}} d^3r \end{aligned} \quad (5.6)$$

where the last line follows from the fact that we are applying the ∇ operator to the positions of the ions $\{\mathbf{R}\}$ not to the electrons $\{\mathbf{r}\}$.

So, instead of having to apply the ∇ operator to the wavefunctions and the Hamiltonian, we only need apply it to the Hamiltonian and we can then calculate the forces using the same expansion coefficients c_k etc as used to calculate the total energy. This is an immense saving in computational effort. If, for some reason, we have to use a position dependent basis-set, then we have an extra contribution to the forces, known as the *Pulay force*, from the effect of applying ∇ to the basis functions.

Having derived the forces on the ions, we can now use this to move them around, either to find directly the geometrical arrangement which minimises the energy (i.e. has zero net force everywhere) or to do molecular dynamics. In this way, we can do study dynamical effects as well, including the effect of finite temperatures. Note that the simplest molecular dynamics ensemble is NVE, that is constant number of particles (N), constant volume (V) and constant energy (E). An experimentally more realistic scenario is NVT

dynamics, where an appropriate thermostat is used to hold the temperature (T) constant and consequently allow some fluctuations in the energy.

5.1.2 Stresses

Just as we can derive the forces from the change in total energy upon varying the ionic positions, we can also derive the stress on the unit cell from the change in total energy upon varying the cell vectors. The details are a bit more complex, as the cell stress is a 3x3 tensor whereas the ionic force is a 3x1 vector, and the cell strain is a 3x3 tensor whereas the ionic displacement is a 3x1 vector.

However, once we have the stress, we can either use it to find directly the cell size and shape which minimises the energy (i.e. has zero stress), or to combine it with the forces to do molecular dynamics with a dynamically varying cell shape. This then enables us to do NPT dynamics, i.e. with constant pressure (P), which is the most common experimental situation.

5.1.3 Charge Density

In a single particle system, we are used to calculating the wavefunction and associating the probability of finding the particle in a small volume dV at a point \mathbf{r} with the wavefunction as

$$P(\mathbf{r} \rightarrow \mathbf{r} + dV) = |\psi(\mathbf{r})|^2 dV \quad (5.7)$$

and

$$1 = \int P(\mathbf{r}) d^3r \quad (5.8)$$

This is not so useful when we have multiple particles, particularly in a condensed matter system where there may be a very large number in a macroscopic sample (say $\sim 10^{23}$ in a mole of substance). A more useful quantity, which is experimentally measurable and closely related to the probability density, is the charge density $n(\mathbf{r})$ where

$$N = \frac{1}{V} \int n(\mathbf{r}) d^3r \quad (5.9)$$

and N is the number of particles in the volume V (for example, in the unit cell of a crystal).

The charge density can be calculated from the wavefunction of the system, but as we shall see in later lectures, it is also a fundamental quantity in its own right. In fact, specifying the charge density uniquely determines the state of the system, and there is a unique charge density that corresponds to the ground state of the system and therefore which minimises the total energy of the system. It is experimentally measurable using various scattering techniques.

5.2 Applications

In the handout there are many examples of different theoretical calculations of experimentally verifiable quantities which will be discussed in the lecture. A variety of different theoretical techniques are used to calculate the total energy which is the basis for all these calculations - primarily, the Hartree-Fock method (which we shall discuss in more detail in a later lecture) and Density Functional Theory (in the lecture following Hartree-Fock). As such, the calculations presented all represent properties of the ground state of the system.

It should be noted that there are many other quantities of interest that can be calculated, such as optical properties, but that in general these are properties of excited states of the system. As such, they can sometimes be calculated using modifications to the above techniques, but there are some technical difficulties associated with the (often) lack of a variational principle for excited states.

5.3 Final comments

A few final points to highlight:

- Many quantities of interest are properties of the ground state of the system and as such are accessible through calculation of the total energy.
- If the calculation is a first-principles, parameter-free calculation (apart from specifying the types of atom and their masses) then it is often known as an *ab initio* calculation.
- It is often possible to calculate the forces on the ions from the total energy and hence both relax structures to equilibrium, and also do molecular dynamics. Similarly, for periodic systems, the stress on the unit cell can be calculated which enables the shape of the unit cell to be determined and for molecular dynamics with pressure control.

5.4 Further reading

- Hellmann-Feynman Theorem in “Methods of Electronic Structure Calculations” by M. Springborg, Chapter 20
- Example applications in many chapters of “Methods of Electronic Structure Calculations” by M. Springborg

