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Reformulated Problems

A Nobel prize was awarded for the invention of a method to calculate the quantum mechanical ground state of many-electron systems. This was based, not on the invention of a new numerical method or algorithm, nor on the implementation of one, but on an approximate reformulation of the governing equation. This last chapter illustrates the power of reformulating equations to make them amiable to numerical solution.

16.1 Three and a half formulations of electrostatics

The electric field in a static situation obeys the equations

$$\begin{aligned}\nabla \cdot \mathbf{E} &= \rho/\epsilon_0 \\ \nabla \times \mathbf{E} &= 0 \quad (\text{formulation 1})\end{aligned}$$

Here, ρ is the charge density and ϵ_0 a universal physical constant. These are four coupled partial differential equations (PDEs). Since the curl of \mathbf{E} vanishes, it is possible to introduce the electric potential Φ , and then obtain the electric field as the derivative of the potential $\mathbf{E} = -\nabla\Phi$, thus

$$\nabla^2\Phi = -\rho/\epsilon_0 \quad (\text{formulation 2})$$

The potential is a scalar function, and hence easier to deal with than the three component vector \mathbf{E} . This simple reformulation leads to a single partial differential equation, and hence simplifies the problem tremendously. Instead of solving four coupled PDEs we solve one PDE.

In empty space, the potential obeys $\nabla^2\Phi = 0$; when the right-hand side vanishes it is called the “Laplace equation”; when there is a source term it is called “Poisson equation”.

There is yet another formulation of electrostatics. It is well known that the electric potential of a point charge is given by $\Phi = 1/(4\pi\epsilon_0)q/r$, where q is the electric charge and r is the distance between the point charge and the point where the potential is evaluated. The Laplacian of this expression is zero everywhere, $\nabla^2\Phi = 0$, except at the origin. For a collection of point charges the potentials add up, $\Phi(\mathbf{r}) = 1/(4\pi\epsilon_0)\sum_j q_j/|\mathbf{r} - \mathbf{r}_j|$, where the sum is over point charges with charge q_j at position \mathbf{r}_j . Generalizing further, for a continuous charge distribution the potential can be expressed by integrating over all sources,

$$\Phi(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (\text{formulation 3})$$

This was a physically guided derivation; with a bit of calculus it could be verified that this integral indeed satisfies the Poisson equation, and is thus equivalent to the previous formulation. Each of the three formulations describes the same physics. The integral is an alternative to solving the partial differential equation.

Such methods can be constructed whenever a PDE can be reformulated as an integral over sources. (Another example is the integral solution to the diffusion equation given in section 15.2.) If the potential is required at only a few locations in space or if the charges occupy only a small portion of space, the integral may be computationally the most efficient formulation.

In addition to exact reformulations, there may be *approximate* formulations of the problem that drastically reduce its computational complexity. For example, the gravitational force from a distant star cluster may be approximated by that of its center of mass. If the approximation is a good one, this can be game changer. After all, because of roundoff, no numerical result is exact, so fundamentally an approximation is not necessarily inferior.

16.2 Schrödinger equation*

The spatial behavior of microscopic matter, of atoms and electrons, is described by the Schrödinger equation, which is a partial differential equa-

tion for the complex-valued wavefunction $\psi(\mathbf{r})$ in a potential $V(\mathbf{r})$. Both are functions of the three-dimensional position vector \mathbf{r} . In its time-independent form

$$-\frac{1}{2}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

and the wavefunction must be normalized such that the integral of $|\psi(\mathbf{r})|^2$ over all space yields 1, $\int |\psi(\mathbf{r})|^2 d\mathbf{r} = 1$. This is a boundary value problem, which may have solutions only for certain values of energy E (which is how energy quantization comes about).

The energy is obtained by multiplying the above expression with the complex conjugate ψ^* and integrating both sides of the equation. For the ground state, the energy E is a minimum (Rayleigh-Ritz variational principle). An expression for the ground state energy is

$$E_{\text{gs}} = \min_{\psi} \int \left[-\frac{1}{2}\psi^*\nabla^2\psi + V|\psi|^2 \right] d\mathbf{r}$$

where the minimum is over all normalized complex functions. The principle implies that we can try out various wavefunctions, even some that do not satisfy the Schrödinger equation, but the one with minimum energy is also a solution to the Schrödinger equation.

Here is one way of solving the Schrödinger equation. The wavefunction is written as a sum of functions $\varphi_n(\mathbf{r})$: $\psi(\mathbf{r}) = \sum_n a_n \varphi_n(\mathbf{r})$. If the φ 's are well chosen then the first few terms in the series approximate the wavefunction and more and more terms can make the approximation arbitrarily accurate. Adjusting the coefficients a_n to minimize the energy, analytically or numerically, will provide an approximate ground state.

For two electrons, rather than one, the wavefunction ψ becomes a function of the position of both electrons, but ψ still obeys the Schrödinger equation. There is one additional property that comes out of a deeper physical theory, namely that the wavefunction must obey $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$. This is called the “Pauli exclusion principle,” because it was discovered by physicist Wolfgang Pauli and it implies that the wavefunction for two electrons at the same location vanishes, $\psi(\mathbf{r}, \mathbf{r}) = 0$. For

more than two electrons the wavefunction is antisymmetric with respect to exchange of any pair of electrons.

Suppose we wish to determine the ground state of the helium atom. Since nuclei are much heavier than electrons we neglect their motion, and we neglect all magnetic interactions. The potential due to the electric field of the nucleus is $V(r) = -2e^2/r$, where e is the charge of a proton. In addition, there is also electrostatic repulsion between the two electrons. The Schrödinger equation for the helium atom is

$$\left[\underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2}_T + \underbrace{\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}}_{V_{ee}} \underbrace{-2\frac{e^2}{r_1} - 2\frac{e^2}{r_2}}_{V_{\text{ext}}} \right] \psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

The symbol ∇_1 means the gradient is with respect to the first argument, here the coordinate vector \mathbf{r}_1 . The expressions are grouped into terms that give rise to the kinetic energy T , electron-electron interaction V_{ee} , and the external potential due to the attraction of the nucleus—external from the electron’s point of view, V_{ext} . The Schrödinger equation with this potential cannot be solved analytically, but the aforementioned method of approximation by minimization is still applicable.

A helium atom has only two electrons. A large molecule, say a protein, can easily have tens of thousands of electrons. Since ψ becomes a function of many variables, three for each additional electron, an increasing number of parameters is required to describe the solution in that many variables to a given accuracy. The number of necessary parameters for N electrons is (a few) 3N , where “a few” is the number of parameters desired to describe the wavefunction along a single dimension. The computational cost increases exponentially with the number of electrons. Calculating the ground state of a quantum system with many electrons is computationally unfeasible with the method described.

16.3 Outline of density functional method*

It turns out that energies in the N -electron Schrödinger equation can also be written in terms of the charge density $n(\mathbf{r})$,

$$n(\mathbf{r}) = N \int \dots \int \psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N.$$

The integrals are over all but one of the coordinate vectors, and because of the antisymmetries of the wavefunction it does not matter which coordinate vector is left out. For brevity the integrals over all \mathbf{r} 's can be denoted by

$$\langle \psi | (\text{anything}) | \psi \rangle = \int \dots \int \psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots) (\text{anything}) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N.$$

This notation is independent of the number of electrons. We then have $\langle \psi | V_{\text{ext}} | \psi \rangle = \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$ for the energy of nuclear attraction.

The expression for the total energy becomes

$$E = \langle \psi | T + V_{ee} + V_{\text{ext}} | \psi \rangle = \langle \psi | T + V_{ee} | \psi \rangle + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r}$$

where ψ is a solution to the time-independent multi-electron Schrödinger equation. The ground state can be obtained by minimization over all normalized wavefunctions with the necessary antisymmetry properties. Such trial wavefunctions do not need to satisfy the Schrödinger equation. Of course, the minimization can be restricted to trial wavefunctions with ground state charge density n_{gs} ,

$$E_{\text{gs}} = \min_{\psi | n_{\text{gs}}} \langle \psi | T + V_{ee} | \psi \rangle + \int V(\mathbf{r}) n_{\text{gs}}(\mathbf{r}) d\mathbf{r}$$

The problem splits into two parts

$$E_{\text{gs}} = \min_n \left\{ F[n] + \int V(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\}$$

and $F[n] = \min_{\psi | n} \langle \psi | T + V_{ee} | \psi \rangle$

Hence, the energy E is a function purely of the charge density $n(\mathbf{r})$ and does not need to be expressed in terms of $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$, which would be a function of many more variables. This is known as the Kohn-Hohenberg formulation. The above equations do not tell us specifically how E depends on n , but at least the reduction is possible in principle.

The kinetic energy and self-interaction of the electrons expressed in terms of the charge density, $F[n]$, is called a “density functional,” since functional is the name for a function that takes a function, here the electron density, as an argument. The functional $F[n]$ is independent of the external potential V_{ext} ; it describes how the electrons interact with themselves. Once an expression, or approximation, for $F[n]$ is found, it is possible to determine the ground state energy and charge density by minimizing E with respect to n for a specific external potential. Since n is a function in 3 rather than $3N$ variables, the computational cost of this method no longer increases exponentially with the number of electrons. (It is essential that good approximations to $F[n]$ can be found at a reasonable computational cost, but we will not deal with this here.)

The wavefunction is not determined by this method, but E provides the energy; n provides the size and shape of the molecule, and changes of E with respect to displacements yield the electrostatic forces, such that physically interesting quantities really *are* described in terms of the charge density alone.

This chapter described two different approaches for the same problem, one using the many-electron wavefunction, the other the electron density. With a large number of electrons only the latter method is computationally feasible. The problem was split into an expensive part that describes the electrons by themselves and a computationally cheap part that describes the interaction of the electrons with the external potential. Molecules and solids are built by electronic interactions, and the density functional method is one of the most consequential achievements of computational physics; it was awarded a Nobel prize in chemistry. The key progress has been achieved not by improvements in numerical methods or computing power, but by a sophisticated mathematical reformulation of the equations to be solved.