

UNDERSTANDING ELECTRONIC WAVE FUNCTIONS

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INTRODUCTION

In this article I discuss some aspects of what is known about correlated electronic wavefunctions, in particular what has been learned from quantum Monte Carlo studies of the homogeneous electron gas. First, I motivate the discussion, then briefly give references to the quantum Monte Carlo methods, discuss the pair product wavefunction and its generalization to backflow and three body wavefunctions. Finally, I conclude with some current difficulties in extending these ideas to electrons in an external potential.

Before we dive in, let me open this short review with some philosophy, appropriate to the conference setting. What does it mean to say one understands something about electron correlation? We will take the somewhat controversial position that an important aspect is to understand the many-body wavefunction. The conventional picture, dating back to Bohr and Heisenberg, is that all we should strive to do is to calculate measurable quantities, the response functions, densities and so forth. More recently, density functional theory takes the point of view that the density functional is the main object to understand. The debate goes back to the founders of quantum mechanics with the Copenhagen interpretation arguing that one should just deal with measurable objects. However, many physicists felt that quantum theory become more definite when Schrödinger wrote down his equation and introduced the idea of a wavefunction, leading materialists to hope that the wavefunction was the reality behind quantum mechanics.

If we can, by some means, specify a many-body wavefunction with sufficient accuracy then all matrix elements are determined. The wavefunction contains complete information but it is a complicated $3N$ dimensional function. We will not necessarily be able to compute any properties analytically but they can be calculated straightforwardly using Monte Carlo techniques. The understanding of quantum systems will have been reduced to understanding of classical systems. This is one justification for seeking to determine the many-body wavefunction. It is by no means obvious to me that the

goal of determining the wave function is any more difficult than determining the density functional. Whether or not we can achieve this goal, a challenging intellectual goal is to determine the many body wave function, and is a puzzle of some practical importance.

The many-body wavefunction for N electrons is a $3N$ dimensional antisymmetric function, even if we forget about electron spin. Feynman argued[1] that a completely general understanding is ruled out, simply because the initial conditions require too much information. In quantum mechanics, one is allowed to take any initial conditions on the wavefunction. If each dimension requires a mesh or basis of say 100 functions, the entire function will require 100^{3N} complex numbers. To seek understanding in the general case is hopeless; we have to restrict ourselves to simpler situations: either low-lying eigenstates, or, a possibility more common but not considered here, systems in thermodynamic equilibrium.

Many problems will require the density matrix because, except for isolated non-degenerate systems, the density matrix is more fundamental. For example typical highly excited states are chaotic, and it is expected that the wave function is effectively random. However, the thermal density matrix, at a high or a low temperature, is a smooth function. I will not worry about the difference in this talk, but assume that much of what is written about the wavefunction can be generalized to the many-body density matrices, though that is not always true.

Even given these caveats what does it mean to understand the wavefunction? There are at least two aspects of understanding:

A. Modeling. By this I mean to find an analytically solvable model whose wavefunction is close to the exact wavefunction. One of the earliest successful models in science was the two sphere model of astronomy. This model allows one to correlate various facts with a simple geometrical picture, but fails in calculating precise trajectories of the planets. That was supplanted by the Ptolemaic models, which are more accurate but less understandable. If one has a simple fairly accurate model (*e.g.* Fermi liquid theory or BCS theory) but which is not able to calculate important properties, there is a question of whether we can really claim full understanding. We must beware of models that manage to account for most but not all of the features, since they may turn out to be completely wrong.

B. Practical calculations of electronic systems are essential to many areas of science and technology. We note in a similar vein, that modern science resulted from the need for more accurate astronomical calculations. Copernicus took pains to make clear that he was only introducing a simpler numerical scheme. This argues that the struggle to compute things may itself lead to understanding.

Let us consider to what extent we understand something as simple as the square root of a number? Of course we can determine that $\sqrt{2} = 1.4142135623730950488\dots$. One knows that the digits do not repeat but that is negative information. There are connections to all sorts of mathematical properties of functions (*e.g.* in the complex plane) that are clearly very useful. We have similar understanding of general properties of wavefunctions. Clearly tabulating values of the square root, useful activity a century ago, has little to do with understanding. Now we compute it as we need it. So is understanding wavefunctions simply akin to understanding what the square root button does on a calculator?

One sort of understanding most of us have is the algorithm for calculating \sqrt{x} using pencil and paper. A general procedure involves Newton iteration:

Procedure for square root of y

```
initialize x
repeat
  error = x2-y
  x = x - error/(2x)
while | error | > tolerance
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We find an initial approximation, a procedure for estimating the error and for using this error to make a better approximation. For the square root function, it is not hard to prove that such a procedure must converge if the initial approximation is good enough. In fact, you can easily determine how many iterations you will need for a given number of decimal places. If we come up with a procedure like that for the wavefunction, would that constitute an understanding?

Now, let us return to the problem of understanding the correlated electronic wavefunction. In many cases, the role of the good approximation or model (A) is given by a single determinant wave function, and it accounts for most of the energy. What is difficult in chemistry is that so much accuracy is required that even if the Slater determinant is very good, one must do much better in practice. So, what new terms come in when electrons are correlated?

As mentioned above, one cannot simply make a big real-space table of the wavefunction as that would be too verbose. One systematic improvement for practical calculations (B) is to express the wavefunction as a sum over a complete set of single determinants:

$$\Psi(R) = \sum_{k=1}^L c_k \text{Det}_k(R) \quad (1)$$

with the c_k solved for using a variational procedure. This is known as the Configuration Interaction(CI) method in quantum chemistry. This is clearly an improvement over simply making a big table of wavefunction values since the first term (a mean field description) accounts for much of the physics and the corrections are single particle states, chosen to be low in energy. Perturbation theory allows us in advance to select which k 's will have large coefficients. But does a long list of c_k 's constitute an understanding? The values of c_k are analogous to the digits in the expansion of the square root. The main practical problem with this method is that it is still too verbose as the number of electrons increase because electron correlation is not succinctly expressed in terms of determinants. As $N \rightarrow \infty$ then $L \propto \exp(\kappa N)$. Even with today's computers, 30 fully correlated electrons are difficult to treat to "chemical accuracy". Another problem is size-consistency, namely there is no simple relation between the coefficients for the super- molecule AB to those of the molecules A and B .

I propose the following two guidelines for rating the understandability of wavefunctions:

A. Other things being equal, for example the same error in the energy, a more “understandable” wavefunction has fewer adjustable parameters. It is not clear if we have not really solved anything fundamental with this definition since we now have to define “adjustable parameters”. Adjustable parameters require lengthy calculations to determine their values and are not universal.

B. A purely algorithmic guideline is related the cost of determining a wavefunction value or property to a given accuracy; in other words the speed and memory of a calculator that can compute the value of Ψ . We do not have to write down the wavefunction in a big table; we just have to be able to deliver it on demand quickly. For a more understandable wavefunction, this cost is lower.

QUANTUM MONTE CARLO METHODS

There are several Quantum Monte Carlo methods that can be used either A) to assess the accuracy of a given model or B) to provide a computational tool to determine the wavefunction or one of its expectations.

i) Variational Monte Carlo (VMC), where one samples the square of a trial function as if it were a classical Boltzmann distribution, is a way to determine the properties of a given wavefunction[4]. By optimizing the energy or variance defined as:

$$E_V = \langle \psi | \mathcal{H} | \psi \rangle \quad (2)$$

$$\sigma^2 = \langle \psi | [\mathcal{H} - E_V]^2 | \psi \rangle \quad (3)$$

we can choose the best wave function from a given class. In some cases we can determine how accurate a functional form is. In contrast to methods such as SCF and CI of quantum chemistry, any analytic form can be used as a trial function, the only limitation being the cost and memory of computation.

ii) Diffusion Monte Carlo (DMC) is a way to optimize automatically the wavefunction. It is an exact method for bosonic systems. Thus, it can be used to check on the optimization of VMC and put in all kinds of complicated but positive pieces into the wavefunction. For fermion systems, one typically uses the fixed-node approximation, which gives an upper bound to the ground state energy, the best upper bound consistent with the assumed nodes of the trial function. Exact fermion methods (transient estimate or release node) are useful for small fermion systems but they become exponentially slow as the size of the system grows, because of the fermion sign problem.

iii) Path Integral Monte Carlo (PIMC) is conceptually similar to DMC but determines finite temperature properties. Because there are as yet few numerical applications to low temperature electronic systems I will not discuss this further.

THE PAIR PRODUCT OR SLATER-JASTROW WAVEFUNCTION

In the following sections, I will take the simplest continuum example of a many body system:

non- relativistic particles interacting with a pair potential:

$$\mathcal{H} = -\hbar^2/2m \sum_{i=1}^N \nabla_i^2 + \sum_{i<j} v(r_{ij}). \quad (4)$$

In the electron gas, the particles interacts with the Coulomb potential $v(r) = e^2/r$ where $r_s = a/a_0$ is the only dimensionless parameter $\propto n_e^{-1/3}$. For $r_s > 100$ the stable ground state is a quantum crystal. In the small r_s limit, the electrons become uncorrelated and methods based on perturbing around the free Fermi gas are successful. Solid state systems are in the range of $1 < r_s < 5$.

The almost universal choice for a correlated wavefunction is the pair product or Jastrow function (other examples are the Gutzwiller wavefunction for lattice spin systems and the Laughlin wave function for quantum Hall liquids):

$$\Psi(R) = Det(\phi_k(\mathbf{r}_i)) \exp(-\sum_{i<j} u(r_{ij})) \quad (5)$$

where $u(r)$ is the *correlation factor* and the *orbitals* determined by translational symmetry are plane waves $\phi_k(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}$. \mathbf{k} lies beneath the Fermi surfaces. We know analytically the behavior of the correlation function at both large and small r : in the large limit the elementary excitations are plasmons (Bohm and Pines) and in the small r limit one has the cusp condition on the correlation factor.

Remarkably, for the electron gas there is an analytic form wavefunction having no adjustable parameters, the Gaskell-RPA trial function[2] which has these short and long-range properties. It has a simple form in Fourier space:

$$2u(k) = -1/S_{NI}(k) + \sqrt{1/S_{NI}(k)^2 + 12r_s/k^4}. \quad (6)$$

Here, $S_{NI}(k)$ is the structure function for the Slater determinant. This form gets about 95% of the correlation energy. No better form, even those having lots of adjustable parameters[15], has been found. Other properties such as correlation functions are good. Hence, at this level of accuracy, we understand the wavefunction of the electron gas

Do we understand why the form is so accurate for the electron gas? It turns out that this form is not so accurate on systems which have more than one length scale. Probably it is so accurate for the electron gas because the large and small r behaviors more or less determine everything.

One of the predictions from VMC and DMC calculations with this trial function is that the low density liquid is likely to be a partially spin-polarized liquid between $20 \leq r_s \leq 100$ [3, 5, 6]. Recent experiments have confirmed this ferromagnetism in a solid state system[16]. The ground state prefers to break local spin symmetry and put correlation in a Slater determinant, rather than building up more two body correlation. This is a general rule for highly correlated systems, related to Hund's rules in atoms.

The Wigner crystal

The liquid wavefunction breaks down at very low densities when the system crystallizes. The pair product form using plane wave orbitals predicts crystallization at a

much too low a density. One needs to explicitly break translational symmetry by introducing the lattice symmetry into the wavefunction. Shadow wavefunctions[8] probably would spontaneously give the crystal symmetry without having to put it in, but they are more closely related to the path integral description and are not easy to use for fermion systems. We can break translational symmetry by having the orbitals be Wannier functions localized around the lattice sites, $\{\mathbf{z}_k\}$:

$$\phi_k(r) = f(\mathbf{r} - \mathbf{z}_k). \quad (7)$$

The simplest choice of the orbital is a Gaussian $f(r) = \exp(-cr^2)$, which introduces one additional parameter, c controlling the electron localization. This wavefunction is also very accurate. Using it, VMC and DMC calculations have predicted that Wigner crystallization will occur at $r_s \approx 100$ in 3d and $r_3 \approx 37$ in 2d. Experiments[17] on a clean GaAs/AlGa/As hetero-structure have recently confirmed this prediction in 2d.

Questions remain such as how the system “knows” to break translational symmetry. What would happen in a finite system such as a quantum dot or around a defect to the wavefunction? Path integrals provide a natural way to answer some of these questions computationally but they do not necessarily lead to an understandable wavefunction.

Higher Order Wavefunctions

Why go beyond the pair level of a wavefunction? First of all some properties are completely wrong at the pair level, such as the spin dependent Fermi liquid parameters[13]. Also, we need better nodes for DMC. Feenberg proposed an expansion for the wave function for bosonic systems. Can we do something analogous be done for fermion systems?

In calculating the square root, we iterated an initial guess using the error of the guessed solution to make an improved solution. Let us try to do the same for a function, not just a number. This is the basis for iterative eigenvalue solvers such as the Lanczos method. The problem with directly applying those iterative methods is that one quickly ends up having to represent the complete many-body wavefunction, which is infeasible in many-dimensions and also not understandable. We now describe a method which does not have these drawbacks. Brief accounts of this have appeared elsewhere[13].

The error of a trial function $\phi_n(R)$ is its local or residual energy:

$$E_n(R) = \phi_n^{-1}(R)\mathcal{H}\phi_n(R). \quad (8)$$

If the trial function were exact, the local energy would be constant. The method of using the local energy to correct the trial function is based on the generalized Feynman-Kacs formula[19]: the exact wave function at a point R , is related to the average of the local energy over random walks starting at R and generated using a drift term proportional to $\nabla_i \ln[\phi_n(R)]$.

Let us take as our initial approximation a mean field solution, the Hartree state:

$$\phi_1(R) = \prod_i \chi_i(\mathbf{r}_i). \quad (9)$$

Then the basic iteration is a correction of the form:

$$\phi_{n+1}(R) = \phi_n(R) \exp(-\tilde{E}_n(R)) \quad (10)$$

where \tilde{E} means to smooth the local energy and should really be done by path integrals. In practice, we take the same many-body functional form, but optimize with VMC within that form. Finally, we use the permutation operator to make a proper antisymmetric function:

$$\hat{\phi}_n(R) = \frac{1}{N!} \sum_P (-1)^P \phi_n(PR) \quad (11)$$

Numerically, we have carried out this procedure to third order. For homogeneous systems, at second order one gets the pair product function or Jastrow function. At third order, one generates backflow and polarization terms. Figure (1) shows how the energy and variance of the trial function improve order by order. Third order seems to get about 80% of the energy missing at second order.

Hence this smoothed-local-energy method produces a sequence of increasingly accurate correlated wavefunctions for homogeneous systems. The other system on which it has been tried out is liquid ^3He [22] There is also seems to be quite accurate. At each order, one introduces new one particle functions. At second order, one introduces the correlation factor $u(r)$ determined primarily by the long and short-range properties. At third order one introduces a backflow and polarization functions. Polarization is a bosonic correlation while the backflow dresses the particles and changes the fermion nodes.

The sequence of functions so introduced is understandable in the sense I discussed in the introduction: only a few parameters are needed to specify a $3N$ dimensional function, where N itself is arbitrary $N \gg 1$. We also get computationally feasible functions since computer time needed to estimate some property of the wavefunction is roughly proportional to N^3 . As yet we do not know if this procedure can be continued to higher order and thereby make arbitrarily accurate functions. Also the rôle of the initial state is not known and how can we generate other states such as superconductors, spin and charge density waves.

WAVEFUNCTIONS FOR MOLECULES

The bad news is the accuracy of this type of wavefunction when there is an external potential such as would be created by an array of fixed nuclei. Over the last decade there have been a number of attempts to determine accurate energies for very simple molecules using correlated wavefunctions. We discuss low- Z molecules because the experiments and theory are easier than is possible with extended solids since there are no finite size effects or pseudo-potentials to worry about.

Let us try to generalize the Jastrow pair wavefunction of Eq.(5) to a molecule. The first problem is that the orbitals are not determined by translation symmetry as they are in the uniform systems. In computational quantum chemistry this problem has been extensively worked on; the result has been an established method using an

Figure 1: Variational energy versus the variance of the local energy for 3d electron fluid at a density $r_s = 10$. Each point represents one variational calculation from higher to lower energies: pair product, three-body, backflow, and backflow+three body. The filled triangle is the backflow fixed-node result and the dotted line a linear fit through the points.

expansion of “contracted” Gaussians. This is a practical solution, but the answer is not very understandable. Such orbitals are normally used as the starting points for correlated calculations with VMC or DMC.

When we go to the next order, the correlation factor, $u(\mathbf{r}_i, \mathbf{r}_j)$ becomes a six dimensional function instead of the one dimensional function it is in homogeneous system. The technical difficulty in representing the correlation function becomes very important. The basis set problem of quantum chemistry (what basis set is best for a given problem, which is most compact, fastest etc.) gets correspondingly worse. Eventually this problem will be solved, it is just a difficult technical problem. But the correlation factor is now less understandable than it was for the uniform electron gas because of the number of coefficients that come in.

Even after extensive optimization at the second order, the results are not very good; see Fig.(2). Shown are results with single determinants and multiple determinants, with VMC and DMC calculations. Typical errors for the first row atoms and diatomics are often greater than 1 eV, equivalent to 10,000 K. This is not nearly accurate enough. We have not learned to put in correlation in a wavefunction for something as simple as an atom in an understandable way, if the electron orbitals involve more than one symmetry, *i. e.* if s and p orbitals are both occupied. One does get higher accuracy if one replaces inner electrons with a pseudo-potentials. Hence, the problem seems to be in an inefficient treatment of electron correlation of electrons in different shells. This is a key problem in understanding electron correlation.

CONCLUSIONS

What good have Quantum Monte Carlo methods been in learning about electron correlation? As mentioned earlier, QMC is useful for assessing the quality of a trial function and for providing essentially exact results for simple systems. The impact of QMC has been small in materials science except for homogeneous systems such as the electron gas, very light atoms such as solid hydrogen where no pseudo potentials are needed. Recent calculations with atoms and molecules using pseudo-potentials are starting to have a major impact in calculations for difficult problems in chemistry. Even in simple systems, one is not certain that the right phase (e.g. a paired superconductor) has been found. The following list summarizes some of the correlated properties that have been determined for the e- gas:

- Energy versus density and polarization [5, 7]
- Momentum distribution of the electron gas [15]
- Phase diagram of electron gas [5, 12]
- Static linear response of 2 and 3D electron gas [10]
- Pair correlation and structure functions[15]
- Electron gas surface [9, 11]

Figure 2: The accuracy of quantum Monte Carlo calculations for the total energy of first row atoms and homo-nuclear diatoms. The horizontal axis is the atomic number, the vertical axis is the error in the total energy (relative to experiment). Solid lines are single determinant wave functions, dashed lines are multiple determinants. The upper two curves in each plot are VMC calculations, the lower are DMC calculations[20, 21]

- Fermi liquid parameters [18]

In recent years GPS devices have revolutionized the way we locate our position relative to the earth. The complicated theory and technology to make it work was the result of many years of scientific endeavor, but unimportant to the end user, who is only concerned with its cost and accuracy. When will the day arrive when understanding of electron wavefunctions and the ability to perform routine calculations allow science to make a gadget with the wizardry of a GPS device for quantum physics?

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