One and Two Particle Density Matrices - Definitions

Given the electronic Hamiltonian for an *N* electron system

$$\hat{H} = \sum_{i=1}^{N} \hat{f}(i) + \sum_{i<j}^{N} g(i,j) = \hat{F} + \hat{G}$$

where $\hat{f}(i)$ & $g(i,j)$ are the usual one and two electron operators, the total electronic energy associated with a normalized N electron wave function $\psi(1,2,3,\cdots,N)$ is given by

$$E = \langle \psi | \hat{H} | \psi \rangle = \langle \psi | \hat{F} | \psi \rangle + \langle \psi | \hat{G} | \psi \rangle$$

The expectation value of the one electron operator is

$$\langle \psi | \hat{F} | \psi \rangle = \int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\hat{F}\psi(1,2,3,\cdots,N)$$

while an individual term, say that due to $\hat{f}(1)$ is

$$\langle \psi | \hat{f}(1) | \psi \rangle = \int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\hat{f}(1)\psi(1,2,3,\cdots,N)$$

Using the Pauli Principle we may write

$$\psi(2,1,3,\cdots,N) = -\psi(1,2,3,\cdots,N)$$

and so we have

$$\langle \psi | \hat{f}(1) | \psi \rangle = \int d\tau(2,1,3,\cdots,N)\psi^*(2,1,3,\cdots,N)\hat{f}(1)\psi(2,1,3,\cdots,N)$$

If we now re-label the variables in the integral so that 1 and 2 are interchanged

$$\langle \psi | \hat{f}(1) | \psi \rangle = \int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\hat{f}(2)\psi(1,2,3,\cdots,N) = \langle \psi | \hat{f}(2) | \psi \rangle$$

and in general, for any i,j pairs of electron labels one has

$$\langle \psi | \hat{f}(i) | \psi \rangle = \langle \psi | \hat{f}(j) | \psi \rangle$$

One then has

$$\langle \psi | \hat{F} | \psi \rangle = N\int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\hat{f}(1)\psi(1,2,3,\cdots,N) = N\langle \psi | \hat{f}(1) | \psi \rangle$$

which is of course the consequence of all electrons being indistinguishable. We may treat the two electron expectation value in the same way. Given

$$\langle\psi|\hat{G}|\psi\rangle=\int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\hat{G}\psi(1,2,3,\cdots,N)$$

we note that an individual term has the form

$$\langle\psi|g(1,2)|\psi\rangle=\int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)g(1,2)\psi(1,2,3,\cdots,N)$$

and if we re-label the variable in the integral so that 2 and 3 are interchanged we have

$$\langle\psi|g(1,2)|\psi\rangle=\int d\tau(1,2,3,\cdots,N)\psi^*(1,3,2,\cdots,N)g(1,3)\psi(1,3,2,\cdots,N)$$

and noting that

$$\psi(1,3,2,\cdots,N)=-\psi(1,2,3,\cdots,N)$$

we have

$$\langle\psi|g(1,2)|\psi\rangle=\int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)g(1,3)\psi(1,2,3,\cdots,N)=\langle\psi|g(1,3)|\psi\rangle$$

and so the two electron energy may be written as the interaction between a pair of electrons times the number of pairs in the system.

$$\langle\psi|\hat{G}|\psi\rangle=\int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)\hat{G}\psi(1,2,3,\cdots,N)=\frac{N(N-1)}{2}\langle\psi|g(1,2)|\psi\rangle$$

This results in the energy expression

$$E=\langle\psi|\hat{H}|\psi\rangle=N\langle\psi|\hat{f}(1)|\psi\rangle+\frac{N(N-1)}{2}\langle\psi|g(1,2)|\psi\rangle$$

so the energy is the sum of N one electron contributions and $\frac{N(N-1)}{2}$ pair or two electron interactions.

These expressions may be simplified further. Consider again the two-electron operator

$$\langle\psi|g(1,2)|\psi\rangle=\int d\tau(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N)g(1,2)\psi(1,2,3,\cdots,N)$$

Clearly $g(1,2)$ only operates on coordinate 1 and 2 and so we may integrate over the remaining N-2 variables before we integrate over 1 and 2. Doing this formally we obtain

$$\left\langle \psi \middle| g(1,2) \middle| \psi \right\rangle = \int d\tau(1,2) g(1,2) \int d\tau(3,4,\cdots,N) \psi^*(1,2,3,\cdots,N) \psi(1,2,3,\cdots,N)$$

and if we define

$$\Gamma\left(1,2\middle|1,2\right) = \frac{N(N-1)}{2} \int\int d\tau(3,4,\cdots,N) \psi^*(1,2,3,\cdots,N) \psi(1,2,3,\cdots,N)$$

the two electron operator contribution to the energy is

$$\left\langle \psi \middle| \hat{G} \middle| \psi \right\rangle = \int d\tau(1,2) g(1,2) \Gamma(1,2|1,2).$$

Where the quantity $\Gamma(1,2|1,2)$ is called the two-particle density matrix. Γ is called a matrix because it depends on two indices, 1 & 2.

When we attempt to simplify the expectation value of one electron operator

$$\left\langle \psi \middle| \hat{f}(1) \middle| \psi \right\rangle = \int d\tau(1,2,3,\cdots,N) \psi^*(1,2,3,\cdots,N) \hat{f}(1) \psi(1,2,3,\cdots,N)$$

we have a problem because $\hat{f}(1)$ contains the differential operator $-\frac{1}{2}\nabla_1^2$ and moving $\psi^*(1,2,3,\cdots,N)$ to the right of $\psi(1,2,3,\cdots,N)$ will not work because

$$\hat{f}(1)\psi(1,2,3,\cdots,N)\psi^*(1,2,3,\cdots,N) \neq \psi^*(1,2,3,\cdots,N)\hat{f}(1)\psi(1,2,3,\cdots,N)$$

However if we write

$$\hat{f}(1)\psi(1,2,3,\cdots,N)\psi^*(1',2,3,\cdots,N)\Big|_{1'\to 1} = \psi^*(1,2,3,\cdots,N)\hat{f}(1)\psi(1,2,3,\cdots,N)$$

where we understand the notation $1' \to 1$ as saying that after $\hat{f}(1)$ operates on

$$\psi(1,2,3,\cdots,N)\psi^*(1',2,3,\cdots,N)$$

and before we perform the integration, we allow $1'$ to become 1. We can then rewrite the expectation value of $\hat{F}$ as

$$\left\langle \psi \middle| \hat{F} \middle| \psi \right\rangle = \int_{1'\to 1} d\tau(1)\hat{f}(1)\gamma\left(1,1'\right)$$

where we define the one electron density matrix as

$$\gamma(1,1') = N\int d\tau(2,3,\cdots,N)\psi(1,2,3,\cdots,N)\psi^*(1',2,3,\cdots,N)$$

Accordingly the expectation value of the Hamiltonian becomes

$$E = \langle\psi|\hat{H}|\psi\rangle = \int_{1'\to 1} d\tau(1)\hat{f}(1)\gamma(1,1') + \int d\tau(1,2)g(1,2)\Gamma(1,2|1,2)$$

This remarkably compact expression suggests that one needs considerably less information to calculate the electronic energy than is contained in the N particle wavefunction. If one could determine the one and two particle density matrices without knowing the wavefunction ψ one could determine the energy by integrating over six spatial and two spin coordinates. If we had trial density matrices in the same sense that we have trial wavefunctions and if we could use the variation principle to mold these density matrices as we do wavefunctions then we would obviate the need for ψ altogether. Because we know the boundary conditions on ψ it's relatively easy to write down a trial wavefunction that satisfies these conditions and then use the variation principle to improve the trial function. It's not so simple with γ & Γ because it's not obvious what boundary conditions they must satisfy. Much effort has gone into the search for these boundary conditions but as of now they remain elusive and the primary role of the density matrices is interpretive.