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1 Reduced Density Matrix

1.1 Basics

¹ Generally, we define a partial trace of a matrix by the following. Suppose V and W are two vector spaces of dimension m and n . Let e_1, \dots, e_m be a basis for V , likewise f_1, \dots, f_n for W . Let T be an operator over $V \otimes W$. It's elements can be represented by $t_{kl,ij}$ relative to the basis $e_k \otimes f_l$. The partial trace over W is a linear operator on V defined by

$$b_{k,i} = \sum_j t_{kj,ij}$$

In the context of quantum mechanics, this turns out to be quite useful. Suppose we have a product of Hilbert spaces, V and W , $\mathcal{H} = V \otimes W$. Suppose M is an operator on V , which can be made an operator on $V \otimes W$ by taking $M \otimes \mathbf{1}$. Because $\langle O \rangle = \text{Tr}(\hat{\rho} \hat{O})$, if ρ^V is the reduced density matrix on V , then we'd want

$$\text{Tr}((M \otimes \mathbf{1})\rho) = \text{Tr}(M\rho^V)$$

This is exactly true when $\rho^V = \text{Tr}_W \rho$, the partial trace of ρ over W .

A simple physical example is as follows²: Define a qubit over a 2-dimensional vector space as $|u\rangle = u_0|0\rangle + u_1|1\rangle$. Now consider a second qubit, $|v\rangle$. In order to describe both states simultaneously, we need to move into product space:

$$|u\rangle \otimes |v\rangle = \left(\sum_{\alpha} u_{\alpha} |\alpha\rangle \right) \otimes \left(\sum_{\beta} v_{\beta} |\beta\rangle \right) = \sum_{\alpha, \beta} u_{\alpha} v_{\beta} |\alpha\rangle \otimes |\beta\rangle$$

This form, however, implies that the two qubits are not entangled, i.e. have no correlation. More generally, the state could be entangled:

$$|w\rangle = \sum_{\alpha, \beta} w_{\alpha, \beta} |\alpha\rangle \otimes |\beta\rangle$$

When $\det(w_{\alpha, \beta}) \neq 0$ the state is entangled. The density operator is

$$\begin{aligned} \hat{\rho} &= |w\rangle\langle w| = \sum_{\alpha, \beta, \alpha', \beta'} |\alpha\rangle \otimes |\beta\rangle w_{\alpha, \beta} w_{\alpha', \beta'}^* \langle \beta'| \otimes \langle \alpha'| \\ \hat{\rho}^{(1)} &= \sum_{\alpha, \beta, \alpha', \beta'} |\alpha\rangle \otimes \langle \beta| \beta\rangle w_{\alpha, \beta} w_{\alpha', \beta'}^* \langle \beta'| \beta\rangle \otimes \langle \alpha'| \\ &= \sum_{\alpha, \beta, \alpha'} |\alpha\rangle w_{\alpha, \beta} w_{\alpha', \beta}^* \langle \alpha'| \end{aligned}$$

¹From Wikipedia.org: search "partial trace".

²Example taken from John Stack's (UIUC) 580 homework assignment.

Note the reduced operator now acts on states of the first qubit only.

Now return to our Coulomb hamiltonian. At zero temperature, we also can consider the density matrix, however, it will simply be a projection onto the ground state:

$$\hat{\rho}|_{T=0} = |\Psi_0\rangle\langle\Psi_0|$$

But we may also define a one-body density matrix by tracing out degrees of freedom.

$$\begin{aligned} |\Psi_0\rangle &= \int d^3r_1 \cdots d^3r_N |\mathbf{r}_1\rangle \cdots |\mathbf{r}_N\rangle \Psi_0(\mathbf{r}_1, \cdots, \mathbf{r}_N) \\ \implies \hat{\rho} &= |\Psi_0\rangle\langle\Psi_0| = \int d^3r_1 \cdots d^3r_N d^3r'_1 \cdots d^3r'_N |\mathbf{r}_1\rangle \cdots |\mathbf{r}_N\rangle \Psi_0(\mathbf{r}_1, \cdots, \mathbf{r}_N) \Psi_0^*(\mathbf{r}'_1, \cdots, \mathbf{r}'_N) \langle\mathbf{r}'_1| \cdots \langle\mathbf{r}'_N| \end{aligned}$$

Now trace over the position of all the electrons except one:

$$\begin{aligned} \hat{\rho}^{(1)} &= \int d^3r_1 \cdots d^3r_N d^3r'_1 \cdots d^3r'_N |\mathbf{r}_1\rangle \langle\mathbf{r}_2|\mathbf{r}_2\rangle \cdots \langle\mathbf{r}_N|\mathbf{r}_N\rangle \Psi_0(\mathbf{r}_1, \cdots, \mathbf{r}_N) \Psi_0^*(\mathbf{r}'_1, \cdots, \mathbf{r}'_N) \langle\mathbf{r}'_1| \langle\mathbf{r}'_2|\mathbf{r}_2\rangle \cdots \langle\mathbf{r}'_N|\mathbf{r}_N\rangle \\ &= \int d^3r_1 \cdots d^3r_N d^3r'_1 |\mathbf{r}_1\rangle \Psi_0(\mathbf{r}_1, \cdots, \mathbf{r}_N) \Psi_0^*(\mathbf{r}'_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \langle\mathbf{r}'_1| \\ \implies \hat{\rho}^{(1)}(r, s) &= \int d^3r_2 \cdots d^3r_N \Psi_0(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \Psi_0^*(\mathbf{s}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \end{aligned}$$

This disagrees with Paul Kent's definition in his thesis, which I think is a typo. Probably this doesn't matter for any calculations?

Further, we can express it in a basis of one-body states:

$$\begin{aligned} |\mathbf{r}\rangle &= \sum_i |\phi_i\rangle \phi_i^*(\mathbf{r}) \\ \rho_{ij}^{(1)} &= \langle\phi_i|\hat{\rho}^{(1)}|\phi_j\rangle = \int d^3r d^3r' d^3r_2 \cdots d^3r_N \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}') \Psi_0(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \Psi_0^*(\mathbf{r}'_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \\ \rho^{(1)}(r, r') &= \sum_{ij} \rho_{ij} \phi(r) \phi^*(r') \end{aligned}$$

(note this may be off by a factor of N).

1.2 Special case of Slater Determinants

References: Paul Kent's Thesis

1.2.1 One-body

The one body density matrix can be written down in position space as:

$$\rho^{(1)}(r_1, s_1) = N \int d^3r_2 \cdots d^3r_N \Psi(r_1, \dots, r_N) \Psi^*(s_1, r_2, \dots, r_N).$$

The normalization is such that $\int \rho^{(1)}(r, r) d^3r = N$, i.e. the density integrates to the number of electrons.

The Slater determinant form is, by definition,

$$\Psi(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \sum_{\{i_\alpha\}} \epsilon_{\{i_\alpha\}} \prod_{\alpha} \phi_{i_\alpha}(r_\alpha).$$

Plugging this form into the RDM definition,

$$\begin{aligned} \rho^{(1)}(r_1, s_1) &= \frac{N}{N!} \int d^3r_2 \cdots d^3r_N \sum_{\{i_\alpha, j_\beta\}} \epsilon_{\{i_\alpha\}} \epsilon_{\{j_\beta\}} \prod_{\alpha} \phi_{i_\alpha}(r_\alpha) \phi_{j_\alpha}^*(r_\alpha) \\ &= \frac{1}{(N-1)!} \sum_{\{i_\alpha, j_\beta\}} \epsilon_{\{i_\alpha\}} \epsilon_{\{j_\beta\}} \phi_{i_1}(r_1) \phi_{j_1}^*(s_1) \cdot \prod_{\alpha \neq 1} \int d^3r_\alpha \phi_{i_\alpha}(r_\alpha) \phi_{j_\alpha}^*(r_\alpha) \\ &= \frac{1}{(N-1)!} \sum_{\{i_\alpha, j_\beta\}} \epsilon_{\{i_\alpha\}} \epsilon_{\{j_\beta\}} \phi_{i_1}(r_1) \phi_{j_1}^*(s_1) \cdot \prod_{\alpha \neq 1} \delta_{i_\alpha, j_\alpha}. \end{aligned}$$

The after summing over the j_β indices, the $\delta_{i_\alpha, j_\alpha}$ sets all the orbital indices the same. This is because it sets all the indices except i_1, j_1 the same, but after that, there's only one option left for them to be, which is equal to each other. This squares the Levi-Cevitas and they therefore go away. The sums over the other indices can then cancel the factor in front.

$$\rho^{(1)}(r_1, s_1) = \sum_{i_1} \phi_{i_1}(r_1) \phi_{i_1}^*(s_1).$$

Thus it becomes a simple sum over the orbitals.

1.2.2 Two-body

The case of the 2-RDM is similar, but an extra term arises when evaluating the δ -parts. The definition is now

$$\rho^{(2)}(r_1, r_2, s_1, s_2) = N(N-1) \int d^3 r_3 \cdots d^3 r_N \Psi(r_1, \dots, r_N) \Psi^*(s_1, s_2, r_3, \dots, r_N)$$

I set the normalization to make things work out nicer at the end, but I'm not sure that this is the convention that people use. Following the same steps,

$$\rho^{(2)}(r_1, r_2, s_1, s_2) = \frac{1}{(N-2)!} \sum_{\{i_\alpha, j_\beta\}} \epsilon_{\{i_\alpha\}} \epsilon_{\{j_\beta\}} \phi_{i_1}(r_1) \phi_{i_2}(r_2) \phi_{j_1}^*(s_1) \phi_{j_2}^*(s_2) \prod_{\alpha \neq 1, 2} \delta_{i_\alpha, j_\alpha}.$$

Now all except two indices are set equal. One option for the first set of indices is $i_1 = j_1$ and $i_2 = j_2$, and another option is $i_1 = j_2$ and $i_2 = j_1$. In the first case, the Levi-Cevita symbol squares; in the second case, it squares with a sign change. Summing over the $\{j_\beta\}$ carries out the δ action. The other indices cancel out the factor in front.

$$\begin{aligned} \rho^{(2)}(r_1, r_2, s_1, s_2) &= \sum_{i_1, i_2} [\phi_{i_1}(r_1) \phi_{i_2}(r_2) \phi_{i_1}^*(s_1) \phi_{i_2}^*(s_2) - \phi_{i_1}(r_1) \phi_{i_2}(r_2) \phi_{i_2}^*(s_1) \phi_{i_1}^*(s_2)] \\ &= \sum_{i_1} \phi_{i_1}(r_1) \phi_{i_1}^*(s_1) \sum_{i_2} \phi_{i_2}(r_2) \phi_{i_2}^*(s_2) - \sum_{i_1} \phi_{i_1}(r_1) \phi_{i_1}^*(s_2) \sum_{i_2} \phi_{i_2}(r_2) \phi_{i_2}^*(s_1) \\ &= \rho^{(1)}(r_1, s_1) \rho^{(1)}(r_2, s_2) - \rho^{(1)}(r_1, s_2) \rho^{(1)}(r_2, s_1) \end{aligned}$$

Thus, for this special state, the 2-RDM is expressible in terms of 1-RDM elements.

1.2.3 Different spin case

So far all this analysis has assumed the spins are the same, and therefore the operations are all occurring for the same-spin determinants. In the case that the spin indices of r_1 and r_2 are different, the particles are distinguishable, and therefore should come out more symmetric. The way this comes about mathematically is that now, two Slater determinants are involved. The integrals factor over the two determinants.

$$\begin{aligned} \rho^{(2)}(r_{1,\sigma}, r_{2,\chi}, s_{1,\sigma}, s_{2,\chi}) &= N(N-1) \int d^3 r_3 \cdots d^3 r_N \\ &\quad \times \Psi_\sigma^*(r_{1,\sigma}, \dots, r_{N_\sigma}) \Psi_\chi^*(r_{2,\chi}, \dots, r_{N_\chi}) \Psi_\sigma(s_{1,\sigma}, \dots, r_{N_\sigma}) \Psi_\chi(s_{2,\chi}, \dots, r_{N_\chi}) \\ &= N(N-1) \int d^3 R_\sigma \Psi_\sigma^*(r_{1,\sigma}, \dots, r_{N_\sigma}) \Psi_\sigma(s_{1,\sigma}, \dots, r_{N_\sigma}) \\ &\quad \times \int d^3 R_\chi \Psi_\chi^*(r_{2,\chi}, \dots, r_{N_\chi}) \Psi_\chi(s_{2,\chi}, \dots, r_{N_\chi}) \\ &= \rho^{(1)}(r_{1,\sigma}, s_{1,\sigma}) \rho^{(1)}(r_{2,\chi}, s_{2,\chi}). \end{aligned}$$

Thus, it factors symmetrically, as I suggested.

2 Many-body operators written in second-quantization notation

If we want to express a one-body operator: an operator which can be described with a one-body basis, such as kinetic energy, we can do so as follows:

$$\hat{A} \equiv \sum_{ij} \hat{c}_i^\dagger A_{ij} \hat{c}_j$$

This is because \hat{A} is completely determined by its action on a one-body basis $|\phi_i\rangle \forall i$. Let $|\Omega\rangle$ be the ground (vacuum) state.

$$\begin{aligned}
\langle \phi_{i'} | \hat{A} | \phi_{j'} \rangle &= \langle \phi_{i'} | \sum_{ij} \hat{c}_i^\dagger A_{ij} \hat{c}_j | \phi_{j'} \rangle \\
&= \sum_{ij} \langle \Omega | \hat{c}_{i'} \hat{c}_i^\dagger A_{ij} \hat{c}_j \hat{c}_{j'}^\dagger | \Omega \rangle \\
&= \sum_{ij} \langle \Omega | (\delta_{ii'} - \hat{c}_i^\dagger \hat{c}_{i'}) A_{ij} (\delta_{jj'} - \hat{c}_{j'}^\dagger \hat{c}_j) | \Omega \rangle \\
&= \sum_{ij} \langle \Omega | \delta_{ii'} \delta_{jj'} A_{ij} | \Omega \rangle \\
&= A_{i'j'}
\end{aligned}$$

For two body operators,

$$\hat{A} \equiv \sum_{i_1 i_2 j_1 j_2} \hat{c}_{i_1}^\dagger \hat{c}_{i_2}^\dagger A_{ij} \hat{c}_{j_1} \hat{c}_{j_2}$$

Then in this case,

$$\langle \phi_{i'_1} \otimes \phi_{i'_2} | \hat{A} | \phi_{j'_1} \otimes \phi_{j'_2} \rangle = \sum_{i_1 i_2 j_1 j_2} \langle \Omega | \hat{c}_{i'_1} \hat{c}_{i'_2} \hat{c}_{i_2}^\dagger \hat{c}_{i_1}^\dagger A_{ij} \hat{c}_{j_1} \hat{c}_{j_2} \hat{c}_{j'_1}^\dagger \hat{c}_{j'_2}^\dagger | \Omega \rangle$$

Note that

$$\hat{c}_{j_1} \hat{c}_{j_2} \hat{c}_{j'_2}^\dagger \hat{c}_{j'_1}^\dagger | \Omega \rangle = (\delta_{j_1 j'_1} \delta_{j_2 j'_2} - \delta_{j_1 j'_2} \delta_{j_2 j'_1}) | \Omega \rangle$$

thus, i.e. direct and exchange.

$$\langle \phi_{i_1} \otimes \phi_{i_2} | \hat{A} | \phi_{j_1} \otimes \phi_{j_2} \rangle = A_{i_1 j_1 i_2 j_2} + A_{i_2 j_2 i_1 j_1} - A_{i_1 j_2 i_2 j_1} - A_{i_2 j_1 i_1 j_2}$$

This is just the antisymmetric combination of matrix elements.

2.1 One-body RDM

3 Extended Koopman's theorem

From reference doi: 10.1063/1.461875.

Extended Koopman's theorem comes from a desire to compute the ionization energy from a single exact calculation of a wavefunction, without need to also compute the ionized wavefunction. Defining this energy difference to be

$$\Delta E = E^N - E^{N-1} = \langle \Psi^N | H | \Psi^N \rangle - \frac{\langle \Psi^N | \hat{q}^\dagger H \hat{q} | \Psi^N \rangle}{\langle \Psi^N | \hat{q}^\dagger \hat{q} | \Psi^N \rangle} = - \frac{\langle \Psi^N | \hat{q}^\dagger [H \hat{q}] | \Psi^N \rangle}{\langle \Psi^N | \hat{q}^\dagger \hat{q} | \Psi^N \rangle}$$

Where \hat{q} is a variationally optimized linear combination of the destruction operators of some basis:

$$\hat{q} \equiv \sum_i \alpha_i \hat{c}_i$$

Writing

$$V_{ij} = - \langle \Psi^N | \hat{c}_i^\dagger [\mathcal{H}, \hat{c}_j] | \Psi^N \rangle$$

then \hat{q} is defined by the solution to $(V - \Delta E \rho^1) \alpha = 0$ where ρ^1 is the one-body reduced density matrix. This is just a rewriting of the definition. Putting in a second-quantized hamiltonian, the relation becomes:

$$V_{ij} = \sum_k h_{ik} \rho_{jk}^1 + 2 \sum_{klm} g_{iklm} \rho_{klm}^2$$

where ρ^2 is the two-body reduced density matrix. Source doesn't clarify what h and g are, but they are probably Lucas's ϵ and V corresponding to low energy effective models.

Alternatively, one can compute the energy difference from adding an orbital by

$$C_{ij} = \langle \Psi^N | c_i [\mathcal{H}, c_j^\dagger] | \Psi^N \rangle$$

This represents the difference $E^{N+1} - E^N$.

3.1 Diagonal approximation

If we just take the diagonal elements of V_{ij} and C_{ij} as the eigenvalues mentioned above, we're taking the approximation that the basis elements are the lowest eigenvalues of the Hamiltonian, and that their ordering is correct. Then

$$\begin{aligned} C_{ii} - V_{ii} &= \langle \Psi^N | c_i \mathcal{H} c_i^\dagger | \Psi^N \rangle - \langle \Psi^N | c_i c_i^\dagger \mathcal{H} | \Psi^N \rangle - \left(\langle \Psi^N | c_i^\dagger c_i \mathcal{H} | \Psi^N \rangle - \langle \Psi^N | c_i^\dagger \mathcal{H} c_i | \Psi^N \rangle \right) \\ &= E(N+1) - E(N) - E(N) + E(N-1) \end{aligned}$$

which is akin to the transport gap in a solid: where one excites one electron and moves it far away from the original cell. This creates an extra electron somewhere in the solid, and an extra hole somewhere else.

Some useful checks for doing calculations:

- If c_i is completely unoccupied in $|\Psi^N\rangle$, then $c_i|\Psi^N\rangle = 0$ and $V_{ii} = 0$.
- If c_i is completely occupied in $|\Psi^N\rangle$, then $c_i^\dagger|\Psi^N\rangle = 0$ and $C_{ii} = 0$.
- You can also consider $C_{ii} - V_{jj}$ which corresponds to exciting a electron from orbital j to orbital i , and computing the transport gap.
- Correspondingly, if $C_{ii} - V_{jj} < 0$ for any i or j , then the transport gap is negative, and the system can proliferate excitations, which means something is probably very wrong in the calculation.