Capturing the Interelectron Cusp in the Multiparticle Schrödinger Equation

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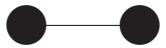
An application for Quantum Mechanics involves computing inner products using geminals. The formulas used to do this have multiple cases and are extremely messy. Organizing the cases graphically helps with figuring out how to compute them and figuring out the cost to compute them. Some cases can be fully reduced graphically. Those that cannot must be put back into a formula and worked by hand.

We start with a formula. We want to represent the formula with some type of picture. We will represent our variables by dots. If two variables are connected by a function, we will represent this connection with an arc or a line depending on the type of function.

Let's say we are given the following formula:

$$\frac{1}{2}\frac{|\mathbb{L}|}{N!}\sum_{a,b}\int\int w_1(|\gamma-\gamma'|)\phi_a(\gamma)\phi_b(\gamma')\begin{vmatrix}\theta_a(\gamma) & \theta_a(\gamma')\\ \theta_b(\gamma) & \theta_b(\gamma')\end{vmatrix} d\gamma d\gamma'.$$

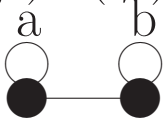
Based on a set of steps, we will be able to create a graphical representation of this formula.

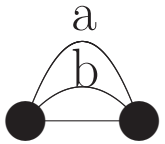
- There are two variables: γ and γ', so we will have two dots.
- There is a function $w_1(|\gamma-\gamma'|)$ connecting the two variables.
  - This type of function we represent as a line.
  - Our current picture is  .

In order to continue, we must expand the determinant. Expanding the determinant and distributing gives us the following formula:

$$\frac{1}{2}\frac{|\mathbb{L}|}{N!}\left(\sum_{a,b}\int\int w_1(|\gamma-\gamma'|)\phi_a(\gamma)\phi_b(\gamma')\theta_a(\gamma)\theta_b(\gamma')d\gamma d\gamma'\right.$$

$$\left.-\sum_{a,b}\int\int w_1(|\gamma-\gamma'|)\phi_a(\gamma)\phi_b(\gamma')\theta_a(\gamma')\theta_b(\gamma)d\gamma d\gamma'\right).$$

In the first summation, $\phi_a(\gamma)\theta_a(\gamma)$ connects γ to itself via arc "a" and $\phi_b(\gamma')\theta_b(\gamma')$ connects γ' to itself via arc "b". This summation gives us 

. In the second summation, $\phi_a(\gamma)\theta_a(\gamma')$ connects γ to γ' via arc "a" and $\phi_b(\gamma')\theta_b(\gamma)$ connects γ' to γ via arc "b". This summation gives us 

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Finding Costs

- We determine which order of operations leads to the least cost.
- N - number of electrons (length of sums)
- M - cost to represent, addition,multiplication or integrate a function of γ
- M_* is the cost to perform a convolution.
- $M < M_* < M^2$ - Convolution costs at least one integration total and at most one integration per output value.
- $N < M$ - the antisymmetry constraint requires the basis set to be at least as large as the number of electrons

Proposition 0.1 *We can contract*

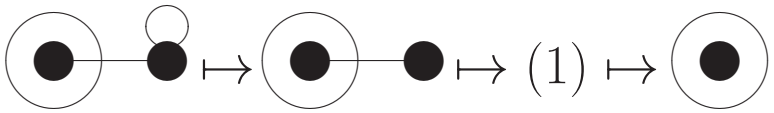
with cost $\mathcal{O}(N^2M + M_*)$. (1)

Proof: This graph corresponds to

$$\int A(\gamma, \cdot)\bar{w}_1(|\gamma - \gamma'|)B(\gamma')d\gamma' \,, \tag{2}$$

where $A(\gamma, \cdot)$ represents the remainder of the graph, and is independent of the variable we are interested in. Integration in γ' costs $\mathcal{O}(M_*)$ and yields $A(\gamma, \cdot)C(\gamma)$. □

Proposition 0.2 *We can contract*



with cost $\mathcal{O}(N^2M + M_*)$.

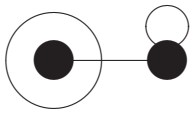
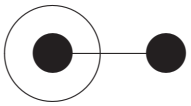
Proof: This graph corresponds to

$$\sum_{a=1}^{N} \int A(\gamma, \cdot)\bar{w}_1(|\gamma - \gamma'|)\bar{\phi}_a(\gamma')\theta_a(\gamma')d\gamma' \,.$$

Summing in a we obtain

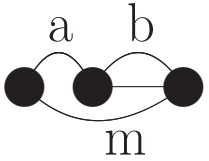
$$A(\gamma, \cdot) \int \bar{w}_1(|\gamma - \gamma'|) \left(\sum_{a=1}^{N} \bar{\phi}_a(\gamma')\theta_a(\gamma') \right) d\gamma'$$
$$= A(\gamma, \cdot) \int \bar{w}_1(|\gamma - \gamma'|)B(\gamma')d\gamma' \,,$$

and we can then apply (1). To compute $B(\gamma')$ costs $\mathcal{O}(NM)$. $\square$

We have a proposition that tells us that if we have a loop at the end of a graph (), we can get rid of the loop (), and then get rid of the variable that had the loop (). In these graphs, the circle surrounding the leftover variable is a shorthand way to represent connections to that variable.

To apply this, if we have  , we can immediately get rid of the loops on the two outside variables, as well as both variables so that we are left with  . There are other propositions to help us reduce further based solely on the picture.

Another application to this would be if we have  , we can immediately get rid of the loop on the left, and then that entire variable, to be left with  . For this example, let's say we cannot reduce further based on a proposition, so we must convert the picture back into a formula to proceed further. Doing this will allow us to create new propositions so we can later reduce more difficult cases graphically.

To put 

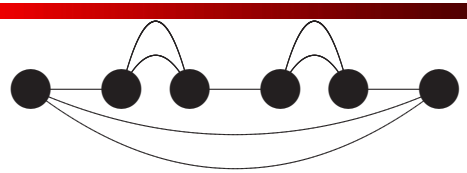
into a formula, we will go step by step as we did for converting a formula to a picture.

- The three dots correspond to three variables. Let's call them γ, γ', and γ''.
- There is a line connecting the second two variables, so we have $w_1(|\gamma' - \gamma''|)$.

- For arc a, it connects the first two variables, so we have $\phi_a(\gamma)\theta_a(\gamma')$.
- Arc b connects the second and third variables, so we have $\phi_b(\gamma')\theta_b(\gamma'')$.
- And arc m connects the third and first variables, giving us $\phi_m(\gamma'')\theta_m(\gamma)$.

Since we have three arcs, we have three summations, and the three variables give us three integrals. Putting this together into one formula gives us

$$\sum_{a,b,m} \int\int\int w_1(|\gamma - \gamma'|)\phi_a(\gamma)\phi_b(\gamma')\phi_m(\gamma'')\theta_a(\gamma')\theta_b(\gamma'')\theta_m(\gamma)d\gamma d\gamma' d\gamma''.$$

Proposition We can compute  with cost $\mathcal{O}(N^2M_* + N^4M)$

Proof:

- The picture above is represented by the formula

$$\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{m=1}^{N}\sum_{n=1}^{N}\sum_{u=1}^{N}\sum_{v=1}^{N}\int\int\int\int\int\int w_1(|\gamma-\gamma'|)w_2(|\gamma''-\gamma'''|)$$
$$w_3(|\tilde{\gamma}-\tilde{\tilde{\gamma}}|)\phi_a(\gamma)\phi_b(\gamma')\phi_m(\gamma'')\phi_n(\gamma''')\phi_u(\tilde{\gamma})\phi_v(\tilde{\tilde{\gamma}})\theta_a(\tilde{\tilde{\gamma}})\theta_v(\gamma)\theta_b(\gamma'')$$
$$\theta_m(\gamma')\theta_n(\tilde{\gamma})\theta_u(\gamma''')$$

- If we first sum over a,it costs $\mathcal{O}(NM^2)$ which is bad.
- So we first intergrate over γ and it costs $\mathcal{O}(N^2M_*)$ which is good.

We rewrite our equation as follows

$$\int \sum_{v=1}^{N}\sum_{n=1}^{N}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{m=1}^{N}\int \left(\int w_1(|\gamma-\gamma'|)\phi_a(\gamma)\theta_v(\gamma)d\gamma\right)\phi_b(\gamma')\theta_m(\gamma')d\gamma'$$
$$\left(\int w_2(|\gamma''-\gamma'''|)\phi_m(\gamma'')\theta_b(\gamma'')d\gamma''\right)\sum_{u=1}^{N}\int\left(\int w_3(|\tilde{\gamma}-\tilde{\tilde{\gamma}}|)\phi_u(\tilde{\gamma})\theta_n(\tilde{\gamma})d\tilde{\gamma}\right)$$
$$\phi_v(\tilde{\tilde{\gamma}})\theta_a(\tilde{\tilde{\gamma}})d\tilde{\tilde{\gamma}}\theta_u(\gamma''')\phi_n(\gamma''')d\gamma'''$$

$$=\int \sum_{v=1}^{N}\sum_{n=1}^{N}\sum_{a=1}^{N}\sum_{b=1}^{N}\sum_{m=1}^{N}\left(\int A_{a,v}(\gamma')\phi_b(\gamma')\theta_m(\gamma')d\gamma'\right)B_{m,b}(\gamma''')$$
$$\sum_{u=1}^{N}\left(\int C_{u,n}(\tilde{\tilde{\gamma}})\phi_v(\tilde{\tilde{\gamma}})\theta_a(\tilde{\tilde{\gamma}})d\tilde{\tilde{\gamma}}\right)\theta_u(\gamma''')\phi_n(\gamma''')d\gamma'''$$

$$= \int \sum_{v=1}^{N} \sum_{n=1}^{N} \sum_{a=1}^{N} \sum_{b=1}^{N} \left(\sum_{m=1}^{N} D_{a,b,m,v} B_{m,b}(\gamma''') \right) \left(\sum_{u=1}^{N} F_{u,n,v,a} \theta_u(\gamma''') \right)$$
$$\phi_n(\gamma''') d\gamma'''$$
$$= \int \sum_{v=1}^{N} \sum_{n=1}^{N} \sum_{a=1}^{N} \left(\sum_{b=1}^{N} E_{a,b,v}(\gamma''') \right) G_{a,n,v}(\gamma''') \phi_n(\gamma''') d\gamma'''$$
$$= \int \sum_{v=1}^{N} \sum_{n=1}^{N} \left(\sum_{a=1}^{N} H_{a,v}(\gamma''') G_{a,n,v}(\gamma''') \right) \phi_n(\gamma''') d\gamma'''$$
$$= \int \sum_{v=1}^{N} \left(\sum_{n=1}^{N} I_{n,v}(\gamma''') \phi_n(\gamma''') \right) d\gamma''' = \int \left(\sum_{v=1}^{N} J_v(\gamma''') \right) d\gamma'''$$
$$= \int K(\gamma''') d\gamma''' = L.$$

Computing $A_{a,v}(\gamma')$, $B_{m,b}(\gamma''')$ and $C_{u,n}(\tilde{\tilde{\gamma}})$ costs $\mathcal{O}(N^2M_*)$;

$D_{a,b,m,v}$, $E_{a,b,v}(\gamma''')$,$F_{u,n,v,a}$ and $G_{a,n,v}(\gamma''')$ costs $\mathcal{O}(N^4M)$;

$H_{a,v}(\gamma''')$ and $I_{n,v}(\gamma''')$ costs $\mathcal{O}(N^3M)$; $J_v(\gamma''')$ costs $\mathcal{O}(N^3M)$;

$K(\gamma''')$ and L cost $\mathcal{O}(NM)$ and hence our total cost is

$\mathcal{O}(N^2M_* + N^4M)$. $\square$

The reductions propositions are helping us to reduce more difficult pictures without doing all the work by hand. This also helps keep our costs down since all of our current propositions are low cost. Our new problem is to reduce graphs with multiple geminal connections. Our propositions do not hold for these problems, so we have to do the reductions by hand, which is proving to be rather tedious.