Notes on the Wavefunction and Local Energy

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1 The Problem

We wish to calculate the local energy, defined as

$$E_{\mathrm{L}} = \frac{1}{\psi} H \psi \tag{1}$$

The Hamiltonian of interest is

$$H = -\frac{1}{2}\sum_{i=1}^{N} \nabla_i^2 - \sum_{\alpha=1}^{M}\sum_{i=1}^{N} \frac{Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}_i|} + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{\alpha<\beta}^{M} \frac{1}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \tag{2}$$

where N is the number of electrons and M is the number of nuclei. The positions of the nuclei are $\mathbf{R}_\alpha$ and the positions of the electrons are $\mathbf{r}_i$.

The wavefunction is going to have the form

$$\psi = d_1 d_2 e^{-U} \tag{3}$$

where d_1 and d_2 are Slater determinants of single particle orbitals, and U is a Jastrow factor containing terms for electron-electron correlation (U_{ee}) and electron-nuclear correlation (U_{ne}). The single particle orbitals are $\phi_i(r)$ and the elements of the Slater matrix are $D_{ij} = \phi_j(r_i)$. The Slater determinant looks like

$$\begin{vmatrix} \phi_1(r_1) & \dots & \phi_n(r_1) \\ \vdots & \ddots & \vdots \\ \phi_1(r_n) & \dots & \phi_n(r_n) \end{vmatrix} \tag{4}$$

We assume that the single particle orbitals depend only on a single coordinate (ie, no backflow).

2 Useful Determinant Properties

We denote the determinant by $|A|$.

The best way (that I know of) to compute the determinant of a matrix is to compute the LU decomposition via LAPACK. The determinant is then the product of the diagonal elements (since both L and U are returned in the same matrix, it doesn't matter whether they belong to L or U). If overflow might be a problem, sum the logarithms of the diagonal elements (one must take the absolute value and keep track of the sign separately in this case.) Note that the permutation vector (for pivoting) must be examined and the sign changed for each permutation. Later we will see that we need the inverse of a matrix, and the LU decomposition is also the first step in computing the inverse. (Note that LAPACK may not be the best choice for very small matrices - one would have to time it.)

Another way to compute the determinant is the expansion by cofactors. This expands the determinant of an $N \times N$ matrix into a sum of determinants of N $(N-1) \times (N-1)$ matrices. As a recursive algorithm for computing the determinant, it is not very efficient, but for analytical manipulations it is very useful for isolating the effect of a single row or column. Define cofactors of a matrix M to be

$$c_{ij} = (-1)^{i+j} \left| M_{ij} \right| \tag{5}$$

where the matrix formed by c_{ij} is called the cofactor matrix. The matrix M_{ij} is an $(N-1) \times (N-1)$ matrix formed by removing row i and column j from A. The determinant of A can then be written as

$$|A| = \sum_j a_{kj} c_{kj} = \sum_i a_{ik} c_{ik} \tag{6}$$

for $k = 1 \ldots N$. The transpose of the cofactor matrix is called the adjoint of A. Now the adjoint is related to the inverse by

$$\text{adj } A = |A| \, A^{-1} \tag{7}$$

As an alternate way to derive the following ratios (and derivatives) of determinants, consider two matrices A and A_1, which differ only in the first row. The rato of the determinants is equal to the determinant of the ratios

$$\frac{|A_1|}{|A|} = \left| \frac{A_1}{A} \right| = \left| A_1 A^{-1} \right| \tag{8}$$

All but pieces involving the first row will give the identity matrix. The first row then will be different from the identity, but the rest of the matrix will be the identity matrix. Then only the element on the diagonal will contribute to the determinant. This element comes from the dot product of the first row of A_1 with the first column of A^{-1}. In some sense, inverting the matrix "interchanges" rows and columns.

3 Ratio of Wavefunctions

In the Metropolis algorithm, we want the ratio of wavefunctions of the trial move and the original position. Typically only one particle is moved, which leads to simplifications [2]. Let us consider moving particle k from r_k to r'_k.

$$\frac{\psi(r'_k)}{\psi(r_k)} = \frac{d(r_k)}{d(r'_k)} e^{-\left[U(r'_k)-U(r_k)\right]} \tag{9}$$

For U_{ee} in the Jastrow factor, we need only sum over $N-1$ distances involving k. For U_{ne}, we will need to sum over all nuclei.

Expand the determinant of $D(r'_k)$ in cofactors about the kth row. Note that then the cofactors have no dependence on r'_k.

$$\begin{aligned}
|D(r'_k)| &= \sum_i \phi_i(r'_k) c_{ki} \\
&= \sum_i \phi_i(r'_k)\, |D(r_k)|\, (D^{-1}(r_k))_{ik} \\
\frac{|D(r'_k)|}{|D(r_k)|} &= \sum_i \phi_i(r'_k) (D^{-1}(r_k))_{ik}
\end{aligned}$$

If a move is accepted, the inverse matrix can be updated in $O(N^2)$ time (rather than $O(N^3)$ for recomputing the inverse). The formula for updating an inverse if only a single row (or column) changes was given by Sherman and Morrison [5]. Let q be the ratio of determinants given above. Row k merely needs to be updated to reflect the new determinant, $D^{-1}_{kj} = D^{-1}_{kj}/q$. The other rows are updated as

$$D^{-1}_{ij} = D^{-1}_{ij} - \frac{D^{-1}_{ik}}{q} \sum_l D^{-1}_{lj} \phi_l(r'_k) \quad i \neq k \tag{10}$$

A more general update formula, where the updating matrix has the form of an outer product of two vectors (rank-1 update?), is given by Bartlett [1]. These formulae are also discussed the book by Fadeev and Fadeeva [3], where they are put together to make the reinforcement method for inverting a matrix

4 Local Energy

Let d be the product of determinants and ∇ represent a $3N$ dimensional gradient. We get

$$\begin{aligned}
\nabla^2 \psi &= \nabla \left[(\nabla d) e^{-U} - (\nabla U) d e^{-U} \right] \\
&= (\nabla^2 d) e^{-U} - 2(\nabla d \cdot \nabla U) e^{-U} - (\nabla^2 U) d e^{-U} + d(\nabla U \cdot \nabla U) e^{-U} \\
\frac{1}{\psi} \nabla^2 \psi &= \frac{\nabla^2 d}{d} - 2(\frac{\nabla d}{d} \cdot \nabla U) - \nabla^2 U + \nabla U \cdot \nabla U \qquad (11)
\end{aligned}$$

Thus the local energy is

$$E_{\mathrm{L}} = \frac{1}{2} \nabla^2 U - \frac{1}{2} \nabla U \cdot \nabla U - \frac{1}{2} \left(\frac{\nabla^2 d}{d} \right) + \left(\frac{\nabla d}{d} \right) \cdot \nabla U + V \tag{12}$$

Also, for smarter VMC sampling and diffusion Monte Carlo we need the quantum force, $F_{\mathrm{Q}} = \nabla \ln |\psi|^2$.

$$F_{\mathrm{Q}} = 2\left(\frac{\nabla d}{d}\right) - 2\nabla U \tag{13}$$

4.1 More general wavefunction

Rather than considering the Jastrow part and the determinants separately, consider the wavefunction as a product of K functions

$$\psi = \prod_{i=0}^{K} \psi_i \tag{14}$$

$$\nabla \psi = \sum_{j=0}^{K} \nabla \psi_j \prod_{i \neq j}^{K} \psi_i \tag{15}$$

$$\nabla^2 \psi = \sum_{j=0}^{K} \nabla^2 \psi_j \prod_{i \neq j}^{K} \psi_i + \sum_{j=0}^{K} \nabla \psi_j \sum_{k \neq j}^{K} \nabla \psi_k \prod_{i \neq k,j}^{K} \psi_i$$

$$\begin{aligned} \frac{1}{\psi}\nabla^2 \psi &= \sum_{j=0}^{K} \frac{1}{\psi_j} \nabla^2 \psi_j + \sum_{j=0}^{K} \sum_{k \neq j}^{K} \frac{\nabla \psi_j}{\psi_j} \cdot \frac{\nabla \psi_k}{\psi_k} && (16) \\ &= \sum_{j=0}^{K} \frac{1}{\psi_j} \nabla^2 \psi_j + 2 \sum_{j=0}^{K} \sum_{k<j}^{K} \frac{\nabla \psi_j}{\psi_j} \cdot \frac{\nabla \psi_k}{\psi_k} && (17) \end{aligned}$$

5 Derivatives of the Determinant

For the gradient with respect to particle k, expand the determinant by cofactors about row k. Then the cofactors have no r_k dependence.

$$\begin{aligned} |D| &= \sum_i \phi_i(r_k) c_{ki} \\ \nabla_k |D| &= \sum_i \left[\nabla_k \phi_i(r_k)\right] c_{ki} \\ \frac{\nabla_k |D|}{|D|} &= \sum_i \left[\nabla_k \phi_i(r_k)\right] D^{-1}_{ik} \\ \frac{\nabla_k^2 |D|}{|D|} &= \sum_i \left[\nabla_k^2 \phi_i(r_k)\right] D^{-1}_{ik} && (18) \end{aligned}$$

6 Derivatives of the Jastrow Factor

We have two terms in the Jastrow factor, U_{ee} and U_{ne}. Now U_{ee} depends on relative particle coordinates, requiring a change of variables. Note that U_{ne} depends only on the electron coordinate (the nuclear coordinate is fixed), so its derivatives are straightforward.

Let u' and u'' be the first and second derivatives of u, respectively. The gradient is

$$\begin{aligned}
\nabla_k U_{ee} &= \nabla_k \sum_{i<j} u_{ee}(|r_i - r_j|) \\
&= \sum_{i<k} \nabla_k u_{ee}(|r_i - r_k|) + \sum_{k<j} \nabla_k u_{ee}(|r_k - r_j|) \\
&= \sum_{i<k} u'_{ee}(r_{ik}) \frac{\mathbf{r_i} - \mathbf{r_k}}{r_{ik}} + \sum_{k<j} -u'_{ee}(r_{kj}) \frac{\mathbf{r_k} - \mathbf{r_j}}{r_{kj}} \\
&= \sum_{i \neq k} u'_{ee}(r_{ik}) \frac{\mathbf{r_i} - \mathbf{r_k}}{r_{ik}} \qquad (19) \\
\nabla_k U_{ne} &= \sum_{\alpha=1}^{M} u'_{ne}(r_{k\alpha}) \frac{\mathbf{r_k} - \mathbf{R}_\alpha}{r_{k\alpha}} \qquad (20)
\end{aligned}$$

The Laplacian is

$$\nabla_k^2 U_{ee} = \sum_{i \neq k} \frac{2}{r_{ik}} u'_{ee}(r_{ik}) + u''_{ee}(r_{ik}) \tag{21}$$

$$\nabla_k^2 U_{ne} = \sum_{\alpha=1}^{M} \frac{2}{r_{k\alpha}} u'_{ne}(r_{k\alpha}) + u''_{ne}(r_{k\alpha}) \tag{22}$$

If we sum over k and note that $r_{ik} = r_{ki}$, then the U_{ee} sum can be written as a sum over pairs

$$\sum_k \nabla_j^2 U_{ee} = 2 \sum_{i<j} \frac{2}{r_{ij}} u'_{ee}(r_{ij}) + u''_{ee}(r_{ij}) \tag{23}$$

7 Cusp Condition

As two Coulomb particles get close, the potential has a $1/r$ singularity. The wavefunction must be of the correct form to cancel this singularity. First, consider an electron and a nucleus. The relevant part of the Schrodinger equation is

$$\left[-\frac{1}{2M} \nabla_n^2 - \frac{1}{2} \nabla_e^2 - \frac{Ze^2}{r} \right] \psi = E\psi \tag{24}$$

where M is the nuclear mass and Z is the nuclear charge. Assume that $M \gg m_e$, so the first term can be ignored. Write the second term in spherical coordinates and we get

$$-\frac{1}{2}\psi'' - \frac{1}{r}\left(Ze^2\psi + \psi'\right) = E\psi \tag{25}$$

In order for the singularity to cancel at small r, the term multiplying $1/r$ must vanish. So we have

$$\frac{1}{\psi}\psi' = -Ze^2 \tag{26}$$

If $\psi = e^{-cr}$ we must have $c = Ze^2$.

For the case of two electrons, the Schrodinger equation is

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{e^2}{r_{12}}\right]\psi = E\psi \tag{27}$$

Switching to relative coordinates $r_{12} = r_1 - r_2$ gives us

$$\left[-\nabla_{12}^2 + \frac{e^2}{r_{12}}\right]\psi = E\psi \tag{28}$$

Equal mass electrons with unlike spins (no antisymmetry requirement) have an extra factor of 1/2 in the cusp condition compared with the electron-nucleus case. So we have $c = -e^2/2$.

In the antisymmetric case, the electrons will be in a relative p state, reducing the cusp condition by 1/2, so $c = -e^2/4$. Having the correct cusp for like spin electrons gains one very little in the energy or variance, since the antisymmetry requirement keeps them apart anyway.

8 Jastrow Factor

The simplest form of a Jastrow factor that satisfies the cusp condition is

$$\begin{aligned} U_{ee} &= -\sum_{i<j} \frac{a_e r_{ij}}{1 + b r_{ij}} \\ U_{ne} &= \sum_{i,\alpha} \frac{Z_\alpha a_n r_{i\alpha}}{1 + b r_{i\alpha}} \end{aligned} \tag{29}$$

We will set $a_e = 1/2$ and $a_n = 1$ to satisfy cusp conditions. Note that b could be potentially different for each pair of particles (b_{ij}). The first and second derivatives are

$$\begin{aligned} U'_{ee} &= -a_e \sum_{i<j} \frac{1}{(1 + b r_{ij})^2} \\ U''_{ee} &= 2a_e \sum_{i<j} \frac{b}{(1 + b r_{ij})^3} \\ U'_{ne} &= a_n \sum_{i,\alpha} \frac{Z_\alpha}{(1 + b r_{i\alpha})^2} \\ U'_{ne} &= -2a_n \sum_{i,\alpha} \frac{Z_\alpha b}{(1 + b r_{i\alpha})^3} \end{aligned}$$

8.1 Additional terms

From a paper by Schmidt and Moskowitz [4], who use the Boys-Handy form for the wavefunction. The terms in the previous section will satisfy the cusp condition. These additional terms will be higher order than linear in r so as not to disturb the cusp condition. Define $\bar{r}$ as

$$\bar{r} = \frac{br}{1+br} \tag{30}$$

First let us look at the $m = 2, n = 0, o = 0$ term

$$U_{ne} = c_2 \bar{r}^2 = c_2 \left(\frac{b_2 r}{1+b_2 r} \right)^2 \tag{31}$$

Derivatives

$$\begin{aligned}
\bar{r}' &= \frac{b}{(1+br)^2} \\
\bar{r}'' &= -\frac{2b^2}{(1+br)^3} \\
U'_{ne} &= 2c_2 \bar{r}\bar{r}' = 2c_2 \frac{b^2 r}{(1+br)^3} \\
U''_{ne} &= 2c_2(\bar{r}'^2 + \bar{r}\bar{r}'') = 2c_2 \frac{(b^2 - 2b^3 r)}{(1+br)^4}
\end{aligned} \tag{32}$$

8.2 Compatibility with periodic boundary conditions

In a periodic box, the wavefunction must be smooth at $L/2$ or there will be a delta function spike in the local energy, which can lead to non-variational energies. The first and second derivatives of the wavefunction should be zero at $L/2$ (although, strictly, we only need the function and its first derivative to be continuous). One approach to ensure these conditions is to use a matching polynomial at some cutoff radius, $r_c \leq L/2$ [2]. Attempts to fix the previous jastrow factors this way seemed not to work - the connection was smooth, but then the polynomial had fairly large fluctuations between r_c and $L/2$. Perhaps adjusting r_c would help.

The other approach is to use a jastrow factor that has the matching conditions built in. The minimum set of conditions is the cusp condition at small r and the two derivative conditions at $r_m \leq L/2$. This can be satisfied with a cubic polynomial. Let $y = r/r_m$. Then we have

$$u(y) = a_1 y + a_2 y^2 + a_3 y^3 \tag{33}$$

where $a_1 = (\text{cusp value}) * r_m$, $a_2 = -a_1$, and $a_3 = a_1/3$.

Variational freedom is gained by adding a general function multiplied by $y^2(y-1)^3$ to preserve the boundary conditions. We choose a sum of Chebyshev polynomials. The wavefunction is then

$$u(y) = a_1(y - y^2 + \frac{1}{3}y^3) + y^2(y-1)^3 \sum_i b_i T_i(2y-1) \tag{34}$$

where the b_i are variational parameters.

For the derivatives, let $F = y^2(y-1)^3$, and $T = \sum_i b_i T_i(2y-1)$. Then

$$\begin{aligned}
u' &= a_1(1 - 2y + y^2)/r_m + F'T + T'F \\
u'' &= a_1(-2 + 2y)/r_m^2 + F''T + T''F + 2F'T' \\
r_m F' &= 2y(y-1)^3 + 3y^2(y-1)^2 \\
r_m^2 F'' &= 2(y-1)^3 + 12y(y-1)^2 + 6y^2(y-1)
\end{aligned} \tag{35}$$

i	$T_i(x)$	$T_i'(x)$	$T_i''(x)$
0	1	0	0
1	x	1	0
2	$2x^2 - 1$	$4x$	4
3	$4x^3 - 3x$	$12x^2 - 3$	$24x$
4	$8x^4 - 8x^2 + 1$	$32x^3 - 16x$	$96x^2 - 16$

To take into account the $2y - 1$ factor in the argument, multiply T_i' by $2/r_m$ and T_i'' by $4/r_m^2$.

Some runs in a box of hydrogens showed that the effect of the polynomials was similar to reducing r_m. Therefore, it would be useful to deal with r_m as a variational parameter. Of course, then we have to handle the constraint $r_m \leq L/2$ during the minimization. The derivatives for u are (let a_0 be the cusp value)

$$\begin{aligned}
\frac{\partial u}{\partial r_m} &= \frac{\partial}{\partial r_m} a_0 \left[x - x^2/r_m + x^3/(3r_m^2) \right] \\
&= a_0 \left[x^2/r_m^2 - \frac{2}{3} x^3/r_m^3 \right] \\
&= a_0 \left[y^2 - \frac{2}{3} y^3 \right]
\end{aligned} \tag{36}$$

$$\begin{aligned}
\frac{\partial^2 u}{\partial r_m^2} &= a_0 \left[-2x^2/r_m^3 + 2x^3/r_m^4 \right] \\
&= \frac{a_0}{r_m} \left[-2y^2 + 2y^3 \right]
\end{aligned} \tag{37}$$

All the cross derivatives will be zero.

The simplest way to take derivatives of the rest is to note the dependence on r_m is solely through $y = x/r_m$.

$$\frac{\partial F}{\partial r_m} = \frac{\partial F}{\partial y} \frac{\partial y}{\partial r_m}$$

$$\begin{aligned}
\frac{\partial^2 F}{\partial r_m^2} &= \frac{\partial^2 F}{\partial y^2}\left(\frac{\partial y}{\partial r_m}\right)^2 + \frac{\partial F}{\partial y}\frac{\partial^2 y}{\partial r_m^2} && (38)\\
\frac{\partial y}{\partial r_m} &= -x/r_m^2 = -y/r_m && (39)\\
\frac{\partial^2 y}{\partial r_m^2} &= 2x/r_m^3 = 2y/r_m^2 && (40)
\end{aligned}$$

9 Single Particle Orbitals

9.1 Floating Gaussian

One form is

$$\phi_l(r) = \exp\left[\frac{-(r-c_l)^2}{w_l^2}\right] \tag{41}$$

For a collection H_2's, $\mathbf{c}_l$ will be put at the center between the two atoms. In periodic boundary conditions, one must use the correct image in computing the center. The following formula seems to work

$$\mathbf{c}_l = \mathbf{r}_1 + \frac{1}{2}\mathrm{PBC}(\mathbf{r}_2 - \mathbf{r}_1) \tag{42}$$

where the vector $r_2 - r_1$ is the minimum image vector.

The derivatives are

$$\begin{aligned}
\nabla\phi_l &= -\frac{2}{w_l^2}(\mathbf{r}-\mathbf{c}_l)\phi_l\\
\nabla^2\phi_l &= \left[\frac{4}{w_l^4}(\mathbf{r}-\mathbf{c}_l)^2 - \frac{6}{w_l^2}\right]\phi_l && (43)
\end{aligned}$$

A more general form is

$$\phi_l(r) = \exp\left[\frac{-(r-c_l)^2}{w_l^2 + v_l\,|r-c_l|}\right] \tag{44}$$

Let $B = w_l^2 + v_l\,|r-c_l|$. Then $B' = v_l$.

The gradient is

$$\begin{aligned}
\nabla\phi_l &= \left[-\frac{2(\mathbf{r}-\mathbf{c}_l)}{B} + \frac{v_l(r-c_l)^2}{B^2}\frac{\mathbf{r}-\mathbf{c}_l}{|r-c_l|}\right]\phi_l\\
&= (\mathbf{r}-\mathbf{c}_l)\left[-\frac{2}{B} + \frac{v_l\,|r-c_l|}{B^2}\right]\phi_l\\
&= \frac{(\mathbf{r}-\mathbf{c}_l)}{B^2}\left[-2w_l^2 - v_l\,|r-c_l|\right]\phi_l && (45)
\end{aligned}$$

Let $\frac{\partial\phi}{\partial r} = A\phi$. Then

$$A = -\frac{2\,|r-c_l|}{B} + \frac{v_l(r-c)^2}{B^2}. \tag{46}$$

$$
\begin{aligned}
\frac{\partial A}{\partial r} &= -\frac{2}{B} + \frac{2v_l\,|r-c_l|}{B^2} + \frac{2v_l\,|r-c_l|}{B^2} - \frac{2v_l^2(r-c)^2}{B^3} \\
&= -\frac{2}{B} + \frac{4v_l\,|r-c_l|}{B^2} - \frac{2v_l^2(r-c)^2}{B^3} \qquad (47) \\
&= -\frac{2}{B} - \frac{2v_l A}{B} \qquad (48)
\end{aligned}
$$

Then the gradient is

$$
\begin{aligned}
\nabla^2\phi_l &= \frac{1}{r^2}\frac{\partial}{\partial r}r^2 A\phi \\
&= \frac{1}{r^2}\left[2rA\phi + r^2\frac{\partial A}{\partial r}\phi + r^2A^2\phi\right] \\
&= \left[\frac{2}{r}A + \frac{\partial A}{\partial r} + A^2\right]\phi \qquad (49)
\end{aligned}
$$

9.1.1 Ellipsoidal Orbitals

We generalize the orbitals so they are no longer spherical, but ellipsoidal. There are two ways to approach it. One way is to keep the orbitals cylindrical and oriented along the bond axis. This leads to two parameters - the width along the axis and the width perpendicular to the axis. The argument in the exponent then becomes

$$
-\gamma_p\left[(\mathbf{r}-\mathbf{c}_l)\cdot\hat{b}\right]^2 - \gamma_\perp\left|(\mathbf{r}-\mathbf{c}_l) - ((\mathbf{r}-\mathbf{c}_l)\cdot\hat{b})\hat{b}\right|^2 \qquad (50)
$$

where $\mathbf{b}$ is the bond vector.

The other, fully general, way is to write the width as a tensor. This leads to 6 parameters - the orientation (3) and the widths along each axis (3). The argument of the exponent then becomes

$$
-(\mathbf{r}-\mathbf{c}_l)^T\cdot\mathbf{\Gamma}\cdot(\mathbf{r}-\mathbf{c}_l) \qquad (51)
$$

where

$$
\Gamma = \begin{pmatrix} \gamma_{11} & \gamma_{12} & \gamma_{13} \\ \gamma_{12} & \gamma_{22} & \gamma_{23} \\ \gamma_{13} & \gamma_{23} & \gamma_{33} \end{pmatrix} \qquad (52)
$$

Or we can always orient along the z axis, use a diagonal Γ and then use rotation matrices that transform the bond axis to the z-axis.

For the derivatives, these have the form $\phi = Be^{-A}$. Thus

$$
\begin{aligned}
\nabla\phi &= \left[\nabla B - B(\nabla A)\right]e^{-A} \qquad (53) \\
\nabla^2\phi &= \left[-\nabla^2 A + (\nabla A\cdot\nabla A)\right]Be^{-A} + \left[\nabla^2 B - 2\nabla A\cdot\nabla B\right]e^{-A} \qquad (54)
\end{aligned}
$$

For simplicity in the derivative formulas, we will replace $(\mathbf{r}-\mathbf{c}_l)$ with $\mathbf{r}$. The tensor form is the easiest to work with.

$$
A = \gamma_{11}r_x^2 + \gamma_{22}r_y^2 + \gamma_{33}r_z^2 + 2\gamma_{12}r_xr_y + 2\gamma_{13}r_xr_z + 2\gamma_{23}r_yr_z \qquad (55)
$$

$$
\begin{aligned}
(\nabla A)_x &= 2\gamma_{11} r_x + 2\gamma_{12} r_y + 2\gamma_{13} rz && (56)\\
(\nabla A)_y &= 2\gamma_{12} r_x + 2\gamma_{22} r_y + 2\gamma_{23} rz && (57)\\
(\nabla A)_z &= 2\gamma_{23} r_x + 2\gamma_{32} r_y + 2\gamma_{33} rz && (58)\\
\nabla^2 A &= 2\gamma_{11} + 2\gamma_{22} + 2\gamma_{33} && (59)
\end{aligned}
$$

A term of the form $B = 1 + cr$, where c is variational parameter, helped the energy of an isolated H_2 quite a bit. It's derivatives are

$$
\begin{aligned}
\nabla B &= c\hat{r}\\
\nabla^2 B &= \frac{2c}{r}
\end{aligned}
$$

We want a rotation matrices such that the bond vector is oriented in the z direction. The current orientation of $\mathbf{b}$ is given by spherical angles $\cos\phi = \frac{x}{\sqrt{x^2+y^2}}$ and $\cos\theta = \frac{z}{\sqrt{x^2+y^2+z^2}}$. First we have to rotate by ϕ around z, and then by θ around y, and that should orient $\vec{b}$ along the z axis.

$$
R_z = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad R_y = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}
$$

$$
R = R_y R_z = \begin{pmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & \sin\theta \\ -\sin\phi & \cos\phi & 0 \\ -\sin\theta\cos\phi & -\sin\theta\sin\phi & \cos\theta \end{pmatrix} \tag{60}
$$

The argument in the exponetial is then

$$
A = \mathbf{r}^T \cdot \mathbf{R}^T \cdot \mathbf{\Gamma} \cdot \mathbf{R} \cdot \mathbf{r} = \mathbf{r}'^T \cdot \mathbf{\Gamma} \cdot \mathbf{r}' = \mathbf{r}^T \cdot \mathbf{\Gamma}' \cdot \mathbf{r} \tag{61}
$$

where $\mathbf{r}' = \mathbf{R} \cdot \mathbf{r}$ and $\Gamma' = R^T \Gamma R$. Derivatives are

$$
\begin{aligned}
\nabla A &= 2R^T \Gamma \cdot \mathbf{r}' && (62)\\
\nabla^2 A &= 2\gamma'_{11} + 2\gamma'_{22} + 2\gamma'_{33} && (63)\\
&= 2\gamma_{11} + 2\gamma_{22} + 2\gamma_{33} && (64)
\end{aligned}
$$

9.2 Atomic Orbitals

Following MoleCU (from looking at the code), we get atomic basis orbitals. Note that $x = \hat{x} \cdot (\mathbf{r} - \mathbf{R})$, and similar for y and z.

$$
\begin{aligned}
\phi_{1s} &= e^{-\gamma|r-R|} && (65)\\
\phi_{2s} &= |r-R|\, e^{-\gamma|r-R|} && (66)\\
\phi_{3s} &= |r-R|^2\, \phi_{1s} && (67)\\
\phi_{2p} &= \{x, y, z\}\phi_{1s} = \{x, y, z\} e^{-\gamma|r-R|} && (68)\\
\phi_{3d} &= \{x^2, y^2, z^2\}\phi_{1s} && (69)\\
\phi_{3d} &= \{xy, yz, xz\}\phi_{1s} && (70)
\end{aligned}
$$

The gradients are

$$\begin{aligned}
\nabla\phi_{1s} &= -\gamma\frac{\mathbf{r}-\mathbf{R}}{|r-R|}e^{-\gamma|r-R|} && (71)\\
\nabla\phi_{2s} &= \frac{\mathbf{r}-\mathbf{R}}{|r-R|}\left(1-\gamma\left|r-R\right|\right)e^{-\gamma|r-R|} && (72)\\
\nabla\phi_{3s} &= 2(\mathbf{r}-\mathbf{R})\phi_{1s}+\left|r-R\right|^2\nabla\phi_{1s}\\
&= (\mathbf{r}-\mathbf{R})\left[2-\gamma\left|r-R\right|\right]e^{-\gamma|r-R|} && (73)\\
\nabla\phi_{2p} &= \hat{x}\phi_{1s}+x\nabla\phi_{1s}\\
&= \left[\hat{x}-x\gamma\frac{\mathbf{r}-\mathbf{R}}{|r-R|}\right]e^{-\gamma|r-R|} && (74)\\
\nabla\phi_{3d} &= 2\mathbf{x}\phi_{1s}+x^2\nabla\phi_{1s}\\
&= \left[2\mathbf{x}-\gamma x^2\frac{\mathbf{r}-\mathbf{R}}{|r-R|}\right]e^{-\gamma|r-R|} && (75)\\
\nabla\phi_{3d} &= (\hat{x}y+\hat{y}x)\phi_{1s}+xy\nabla\phi_{1s}\\
&= \left(\hat{x}y+\hat{y}x-\gamma\frac{\mathbf{r}-\mathbf{R}}{|r-R|}\right)e^{-\gamma|r-R|} && (76)
\end{aligned}$$

For the $2p$ orbitals, only the derivatives for the x oriented orbital are given.

The Laplacians are

$$\begin{aligned}
\nabla^2\phi_{1s} &= \left(\gamma^2-\frac{2\gamma}{|r-R|}\right)e^{-\gamma|r-R|} && (77)\\
\nabla^2\phi_{2s} &= \left(\frac{2}{|r-R|}-4\gamma+\gamma^2\left|r-R\right|\right)e^{-\gamma|r-R|} && (78)\\
\nabla^2\phi_{3s} &= 2\nabla\cdot(\mathbf{r}-\mathbf{R})\phi_{1s}+4(\mathbf{r}-\mathbf{R})\cdot\nabla\phi_{1s}+\left|r-R\right|^2\nabla^2\phi_{1s}\\
&= \left(6-6\gamma\left|r-R\right|+\gamma^2\left|r-R\right|^2\right)e^{-\gamma|r-R|} && (79)\\
\nabla^2\phi_{2p} &= 2\hat{x}\cdot\nabla\phi_{1s}+x\nabla^2\phi_{1s}\\
&= \left[\gamma^2-\frac{4\gamma}{|r-R|}\right]xe^{-\gamma|r-R|} && (80)\\
\nabla^2\phi_{3d} &= 2\phi_{1s}+4\mathbf{x}\cdot\nabla\phi_{1s}+x^2\nabla^2\phi_{1s}\\
&= \left(2+x^2\gamma^2-\frac{6x^2\gamma}{|r-R|}\right)e^{-\gamma|r-R|} && (81)\\
\nabla^2\phi_{3d} &= \nabla^2(xy)\phi_{1s}+2\nabla(xy)\cdot\nabla\phi_{1s}+xy\nabla^2\phi_{1s}\\
&= \left(\gamma^2-\frac{6\gamma}{|r-R|}\right)xye^{-\gamma|r-R|} && (82)
\end{aligned}$$

9.3 Plane Waves

The orbitals are

$$\phi_l(r)=\sum_{j=1}^{N_{\mathrm{PW}}}c_j^l e^{i\mathbf{k}_j\cdot\mathbf{r}} \tag{83}$$

9.4 Compatibility with periodic boundary conditions

As with the jastrow factors, we need to ensure the that the orbitals have the correct boundary conditions at the edge of the box. We want the orbital and its first two derivatives to be zero at $r_m \leq L/2$. This can be accomplished by multiplying the orbital by a cutoff function f_c. One form for f_c is

$$\begin{aligned} f_c &= 1 - e^{-\gamma_c (r-r_m)^2} \\ f_c' &= 2\gamma_c (r-r_m) e^{-\gamma_c (r-r_m)^2} \\ f_c'' &= 2\gamma_c \left[1 - 2\gamma_c (r-r_m)^2\right] e^{-\gamma_c (r-r_m)^2} \end{aligned} \tag{84}$$

$$\begin{aligned} \nabla f_c &= f_c' \hat{r} \\ \nabla^2 f_c &= \frac{2}{r} f_c' + f_c'' \\ &= \gamma_c \left[6 - 4\gamma_c (r-r_m)^2 - 4\frac{r_m}{r}\right] e^{-\gamma_c (r-r_m)^2} \end{aligned} \tag{85}$$

10 Testing

10.1 Numerical Derivatives

It's useful to compute the local energy numerically and compare that to the analytic local energy. This will point out mistakes in coding or deriving. One could compute derivatives of the various pieces for more insight.

The simplest way is to use a 6 point star formula

$$\nabla^2 \psi \approx \frac{1}{h^2} \sum_i^N \left[\psi(R_i \pm h\hat{x}) + \psi(R_i \pm h\hat{y}) + \psi(R_i \pm h\hat{z}) - 6\psi(R_i)\right] \tag{86}$$

For large systems, ψ can get quite large (or small) and over or underflow the floating point representation. Since we ultimately will divide this expression by ψ, the solution is to use the log of ψ and subtract $\log \psi$ before taking the exponential.

10.2 Simple Systems

We can do some simple integrals with Mathematica and compare the output. First, we use $\gamma = \frac{1}{w_l^2} = 0.1332$. For just the orbital (no correlation and no potential) the exact value of the integral is $E = 0.3996$.

For H_2, we can look at the Reynolds paper, with parameters $\gamma = \frac{1}{w_l^2} = 0.1332$ and an e-e jastrow parameter $b = 0.22459$ and an e-n jastrow parameter of $b = 0.317612$. The nuclei are separated by a distance of 1.401 bohr. The give a variational energy of $E = -1.162(1)$. I get $E = -1.160(2)$ from 400 steps per block and 1000 blocks.

For H_3, we can look at the Ceperley paper. The nuclei are linear, with a separation of 1.757 bohr between them. For spin up (with 2 electrons), $\gamma = 0.2085$, and for spin down (with one electron), $\gamma = 0.09889$. The centers of the spin down orbitals are at $c_l = \pm 2.03$. The center of the spin up orbital is at $c_l = 0$. The e-e jastrow parameter is $b = 0.2223$ and the e-n jastrow parameter is $b = .3143$. They give a variational energy of $-1.663(4)$. I get $-1.595(3)$ with 400 steps per block and 1000 blocks.

I have also compared with the Reynolds paper for Li_2 and LiH, and get good agreement.

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