Framework for constructing generic Jastrow correlation factors

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The Jastrow factor

Trial wave function

$$\Psi_{\mathrm{T}}(\mathbf{R}) = e^{J(\mathbf{R})}\Psi_{\mathrm{S}}(\mathbf{R})$$

- e^J improves Ψ_{S} keeping nodes fixed
- e^J compact parametrization of correlations
- e^J well suited for imposing e.g. Kato cusp conditions
- e^J improves statistics of DMC energy accumulation, and accuracy of other DMC expectation values
- Want to be able to try out arbitrary terms; needs change with each system

OMG it's full of terms!

DTN e–e–n term

$$f = \sum_{i<j} \sum_{I} f(r_{iI}; L) f(r_{jI}; L) \sum_{pqr} \gamma_{pqr} r_{ij}^{p} r_{iI}^{q} r_{jI}^{r}$$

DTN-like e–e–e term

$$W = \sum_{i<j<k} f(r_{ij}; L) f(r_{ik}; L) f(r_{jk}; L) \sum_{pqr} \omega_{pqr} r_{ij}^{p} r_{ik}^{q} r_{jk}^{r}$$

Boys-Handy-like e–e–n–n term

$$J = \sum_{i<j} \sum_{I<J} {\sum_{pqrst}}' c_{pqrst} \tilde{r}_{ij}^{p} \tilde{r}_{iI}^{q} \tilde{r}_{iJ}^{r} \tilde{r}_{jI}^{s} \tilde{r}_{jJ}^{t}$$

Rules of the game

- Sum of terms:
  $$J = J_{\mathrm{e-e}} + J_{\mathrm{e-n}} + J_{\mathrm{e-e-n}} + \ldots =$$
  $$= J_{20} + J_{11} + J_{21} + \ldots$$

- Build from two-body functions and two-body relationships:
  - e–e basis functions: $\Phi_{\nu}^{P}(\mathbf{r})$
    e–n basis functions: $\Theta_{\mu}^{S}(\mathbf{r})$
  - Electron-electron dependency index P
    Electron-nucleus dependency index S

Basic information

- System has N electrons and M nuclei
- $J_{n,m}$ correlates n electrons and m nuclei
- Choose basis functions Φ and Θ
- Define particle relationships:

$$\underline{\mathrm{P}} = \begin{pmatrix} 0 & P_{1,2} & \dots & P_{1,N} \\ P_{1,2} & 0 & \dots & P_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ P_{1,N} & P_{2,N} & \dots & 0 \end{pmatrix} \qquad \underline{\mathrm{S}} = \begin{pmatrix} S_{1,1} & \dots & S_{1,M} \\ \vdots & & \vdots \\ S_{N,1} & \dots & S_{N,M} \end{pmatrix}$$

Mental note

Matrices naturally represent two-body building blocks

Jastrow term as sum over n-electron, m-nucleus groups

Let $\mathbf{i} = (i_1\ i_2\ \ldots\ i_n)$ and $\mathbf{I} = (I_1\ I_2\ \ldots\ I_m)$.

Definition of $J_{n,m}$

$$J_{n,m} = \frac{1}{n!m!} \sum_{\mathbf{i}}^{N} \sum_{\mathbf{I}}^{M} J_{n,m}(\mathbf{i}, \mathbf{I})$$

Or equivalently...

$$J_{n,m} = \sum_{\mathbf{i}}^{\text{s.v.}} \sum_{\mathbf{I}}^{\text{s.v.}} J_{n,m}(\mathbf{i}, \mathbf{I})$$

where s.v. $\equiv$ "sorted vector", e.g. $i_1 < i_2 < \ldots < i_n$.

Matrices for n-electron, m-nucleus group $\{\mathbf{i},\mathbf{I}\}$

e–e expansion-index and dependency-index matrices

$$\underline{\nu}(\mathbf{i}) = \begin{pmatrix} 0 & \nu_{i_1 i_2} & \cdots & \nu_{i_1 i_n} \\ \nu_{i_1 i_2} & 0 & \cdots & \nu_{i_2 i_n} \\ \vdots & \vdots & \ddots & \vdots \\ \nu_{i_1 i_n} & \nu_{i_2 i_n} & \cdots & 0 \end{pmatrix} \qquad \underline{\mathrm{P}}(\mathbf{i}) = \begin{pmatrix} 0 & P_{i_1 i_2} & \cdots & P_{i_1 i_n} \\ P_{i_1 i_2} & 0 & \cdots & P_{i_2 i_n} \\ \vdots & \vdots & \ddots & \vdots \\ P_{i_1 i_n} & P_{i_2 i_n} & \cdots & 0 \end{pmatrix}$$

e–e basis-function matrix

$$\underline{\Phi}^{\underline{\mathrm{P}}}_{\underline{\nu}}(\mathbf{i}) = \begin{pmatrix} 0 & \Phi^{P_{i_1 i_2}}_{\nu_{i_1 i_2}}(\mathbf{r}_{i_1 i_2}) & \cdots & \Phi^{P_{i_1 i_n}}_{\nu_{i_1 i_n}}(\mathbf{r}_{i_1 i_n}) \\ \Phi^{P_{i_1 i_2}}_{\nu_{i_1 i_2}}(\mathbf{r}_{i_2 i_1}) & 0 & \cdots & \Phi^{P_{i_2 i_n}}_{\nu_{i_2 i_n}}(\mathbf{r}_{i_2 i_n}) \\ \vdots & \vdots & \ddots & \vdots \\ \Phi^{P_{i_1 i_n}}_{\nu_{i_1 i_n}}(\mathbf{r}_{i_n i_1}) & \Phi^{P_{i_2 i_n}}_{\nu_{i_2 i_n}}(\mathbf{r}_{i_n i_2}) & \cdots & 0 \end{pmatrix}$$

Matrices for n-electron, m-nucleus group $\{\mathbf{i},\mathbf{I}\}$

e–n expansion-index and dependency-index matrices

$$\underline{\mu}(\mathbf{i},\mathbf{I}) = \begin{pmatrix} \mu_{i_1 I_1} & \cdots & \mu_{i_1 I_m} \\ \vdots & & \vdots \\ \mu_{i_n I_1} & \cdots & \mu_{i_n I_m} \end{pmatrix} \qquad \underline{\mathrm{S}}(\mathbf{i},\mathbf{I}) = \begin{pmatrix} S_{i_1 I_1} & \cdots & S_{i_1 I_m} \\ \vdots & & \vdots \\ S_{i_n I_1} & \cdots & S_{i_n I_m} \end{pmatrix}$$

e–n basis-function matrix

$$\underline{\Theta}^{\underline{\mathrm{S}}}_{\underline{\mu}}(\mathbf{i},\mathbf{I}) = \begin{pmatrix} \Theta^{S_{i_1 I_1}}_{\mu_{i_1 I_1}}(\mathbf{r}_{i_1 I_1}) & \cdots & \Theta^{S_{i_1 I_m}}_{\mu_{i_1 I_m}}(\mathbf{r}_{i_1 I_m}) \\ \vdots & & \vdots \\ \Theta^{S_{i_n I_1}}_{\mu_{i_n I_1}}(\mathbf{r}_{i_n I_1}) & \cdots & \Theta^{S_{i_n I_m}}_{\mu_{i_n I_m}}(\mathbf{r}_{i_n I_m}) \end{pmatrix}$$

The Jastrow factor

Definition of $J_{n,m}(\mathbf{i},\mathbf{I})$ [u.t.≡"upper triangular"]

$$J_{n,m}(\mathbf{i},\mathbf{I}) = \sum_{\underline{\nu}}^{\text{u.t.}} \sum_{\underline{\mu}} \lambda_{\underline{\nu}\underline{\mu}}^{\mathrm{P}\mathrm{S}} \prod_{\underline{\nu}}^{\text{u.t.}} \Phi_{\underline{\nu}}^{\mathrm{P}} \prod \Theta_{\underline{\mu}}^{\mathrm{S}}$$

- Now deduce properties of $J_{n,m}(\mathbf{i},\mathbf{I})$ from two-body properties

Symmetry properties

- Electron interchange represented by permutation matrix $\underline{\mathrm{A}}$, e.g.,

$$\underline{\mathrm{A}}\mathbf{i} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} i_1 \\ i_2 \\ i_3 \end{pmatrix} = \begin{pmatrix} i_1 \\ i_3 \\ i_2 \end{pmatrix}$$

- Nucleus interchange represented by permutation matrix $\underline{\mathrm{B}}$, e.g.,

$$\underline{\mathrm{B}}\mathbf{I} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} I_1 \\ I_2 \\ I_3 \end{pmatrix} = \begin{pmatrix} I_3 \\ I_2 \\ I_1 \end{pmatrix}$$

Then...

How does $J_{n,m}(\underline{\mathrm{A}}\mathbf{i}, \underline{\mathrm{B}}\mathbf{I})$ relate to $J_{n,m}(\mathbf{i}, \mathbf{I})$?

Symmetry properties

Symmetry constraint

$$\lambda^{\underline{\mathrm{P}}(\mathbf{i}),\underline{\mathrm{S}}(\mathbf{i},\mathbf{I})}_{\underline{\nu},\underline{\mu}} = \gamma\left[\underline{\Phi}^{\mathrm{P}}_{\underline{\nu}}(\mathbf{i}),\underline{\mathrm{A}}\right]\lambda^{\underline{\mathrm{A}}\,\underline{\mathrm{P}}(\mathbf{i})\,\underline{\mathrm{A}}^{\mathrm{T}},\underline{\mathrm{A}}\,\underline{\mathrm{S}}(\mathbf{i},\mathbf{I})\,\underline{\mathrm{B}}^{\mathrm{T}}}_{\underline{\mathrm{A}}\,\underline{\nu}\,\underline{\mathrm{A}}^{\mathrm{T}},\underline{\mathrm{A}}\,\underline{\mu}\,\underline{\mathrm{B}}^{\mathrm{T}}}$$

- Parameters whose superindices are permutations of the same $\{\tilde{\underline{\mathrm{P}}},\tilde{\underline{\mathrm{S}}}\}$ (*signature*) are said to be in same *parameter channel*
- $\Phi^{P}_{\nu}(\mathbf{r})$ either symmetric or antisymmetric, and

$\gamma = \pm 1$

$$\gamma\left[\underline{\Phi}^{\mathrm{P}}_{\underline{\nu}}(\mathbf{i}),\underline{\mathrm{A}}\right] = \frac{\prod^{\mathrm{u.t.}}\underline{\mathrm{A}}\,\underline{\Phi}^{\mathrm{P}}_{\underline{\nu}}(\mathbf{i})\,\underline{\mathrm{A}}^{\mathrm{T}}}{\prod^{\mathrm{u.t.}}\underline{\Phi}^{\mathrm{P}}_{\underline{\nu}}(\mathbf{i})} = \pm 1$$

Constraints at coalescence points

Expansion around coalescence point

$$J(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} J^{(l,m)}$$

$$J^{(l,m)} = f_{l,m}(r) Y_{l,m}(\theta, \phi)$$

$$f_{l,m}(r) \approx f_{l,m}(0) + f'_{l,m}(0) r + f''_{l,m}(0) r^2/2$$

Gradient and Laplacian are finite, so...

$$f_{l,m}(0) = 0 \quad \text{if } l \neq 0$$

$$f'_{l,m}(0) = 0 \quad \text{if } l \neq 1$$

Constraints at coalescence points

e–e Kato cusp condition [n.c.≡"no contribution", o.c.≡"one contribution"]

$$\sum_{\underline{\nu}}^{\text{u.t.,o.c.}} \sum_{\underline{\mu}}^{\text{n.c.}} \lambda_{\underline{\nu},\underline{\mu}}^{\underline{P},\underline{S}} \left[\frac{\partial \mathscr{P}_{0,0}\left[\Phi_{\nu_{ij}}^{P_{ij}}(\mathbf{r}_{ij})\right]}{\partial r_{ij}} \right]_{r_{ij}=0} = \Gamma_{ij}$$

Analiticity at e–e coalescence point [e.p.≡"equal product"]

$$\sum_{\underline{\nu}}^{\text{u.t.,e.p.}} \sum_{\underline{\mu}}^{\text{e.p.}} \lambda_{\underline{\nu},\underline{\mu}}^{\underline{P},\underline{S}} \left[\mathscr{P}_{l,m}\left[\Phi_{\nu_{ij}}^{P_{ij}}(\mathbf{r}_{ij})\right] \right]_{r_{ij}=0} = 0 \quad (l \neq 0)$$

$$\sum_{\underline{\nu}}^{\text{u.t.,e.p.}} \sum_{\underline{\mu}}^{\text{e.p.}} \lambda_{\underline{\nu},\underline{\mu}}^{\underline{P},\underline{S}} \left[\frac{\partial \mathscr{P}_{l,m}\left[\Phi_{\nu_{ij}}^{P_{ij}}(\mathbf{r}_{ij})\right]}{\partial r_{ij}} \right]_{r_{ij}=0} = 0 \quad (l \neq 1)$$

Constraints at coalescence points

e–n Kato cusp condition [n.c.≡"no contribution", o.c.≡"one contribution"]

$$\sum_{\underline{\nu}}^{\text{u.t.,n.c.}} \sum_{\underline{\mu}}^{\text{o.c.}} \lambda_{\underline{\nu},\underline{\mu}}^{\underline{\mathrm{P}},\underline{\mathrm{S}}} \left[\frac{\partial \mathscr{P}_{l,m}\left[\Theta_{\mu_{iI}}^{S_{iI}}(\mathbf{r}_{iI})\right]}{\partial r_{iI}} \right]_{r_{iI}=0} = \Gamma_{iI}$$

Analiticity at e–n coalescence point [e.p.≡"equal product"]

$$\sum_{\underline{\nu},\underline{\mu}}^{\text{u.t.,e.p.}} \lambda_{\underline{\nu},\underline{\mu}}^{\underline{\mathrm{P}},\underline{\mathrm{S}}} \left[\mathscr{P}_{l,m}\left[\Theta_{\mu_{iI}}^{S_{iI}}(\mathbf{r}_{iI})\right]\right]_{r_{iI}=0} = 0 \quad (l \neq 0)$$

$$\sum_{\underline{\nu},\underline{\mu}}^{\text{u.t.,e.p.}} \lambda_{\underline{\nu},\underline{\mu}}^{\underline{\mathrm{P}},\underline{\mathrm{S}}} \left[\frac{\partial \mathscr{P}_{l,m}\left[\Theta_{\mu_{iI}}^{S_{iI}}(\mathbf{r}_{iI})\right]}{\partial r_{iI}} \right]_{r_{iI}=0} = 0 \quad (l \neq 1)$$

Indexing

- $1 \leq \nu \leq p$ and $1 \leq \mu \leq q$ by default
- Factorize cut-off function (if applicable):
  $\Phi^P_\nu = f^P \phi^P_\nu$ and $\Theta^S_\mu = f^S \theta^S_\mu$
- Can add $\nu = 0$ and/or $\mu = 0$ and define $\Phi^P_0 = \Theta^S_0 = 1$
- Can introduce *indexing constraints* (i.e., skip over index sets):
  - Efficiency
  - Specialized functional forms (e.g., dot products)

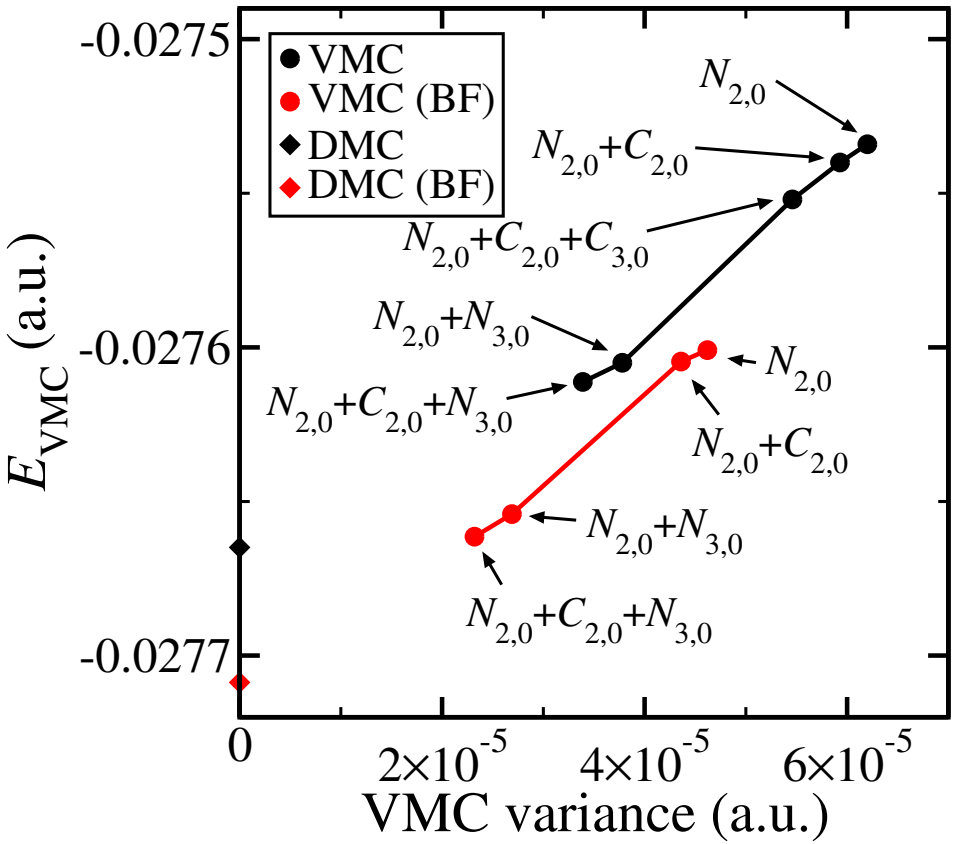
Usage

Using CASL (CASINO serialization language):

```
JASTROW:
  TERM 1:
    Rank: [ 2, 0 ]
    e-e basis:
      Type: cosine
      Order: 2
      Constants:
        Star 1:
          G_1:  [ 0, 0, 0 ]
        Star 2:
          G_1:  [ 0, 0, 1 ]
          G_2:  [ 0, 1, 0 ]
          G_3:  [ 1, 0, 0 ]
    Rules:  [ 1-1=2-2 ]
  TERM 2:
    Rank: [ 2, 1 ]
    e-e basis:
      Type: r/(r^b+a) power
      Order: 5
      Parameters:
        Channel 1-1:
          a: [ limits: [ 0.500000000000000, 20.0000000000000 ],
               1.99161011824704, optimizable ]
          b: [ limits: [ 1.05000000000000, 5.00000000000000 ],
               1.36525793238957, optimizable ]
    Rules: [ 1-1=2-2, 1-n1=2-n1, n1=n2=n3=n4 ]
```

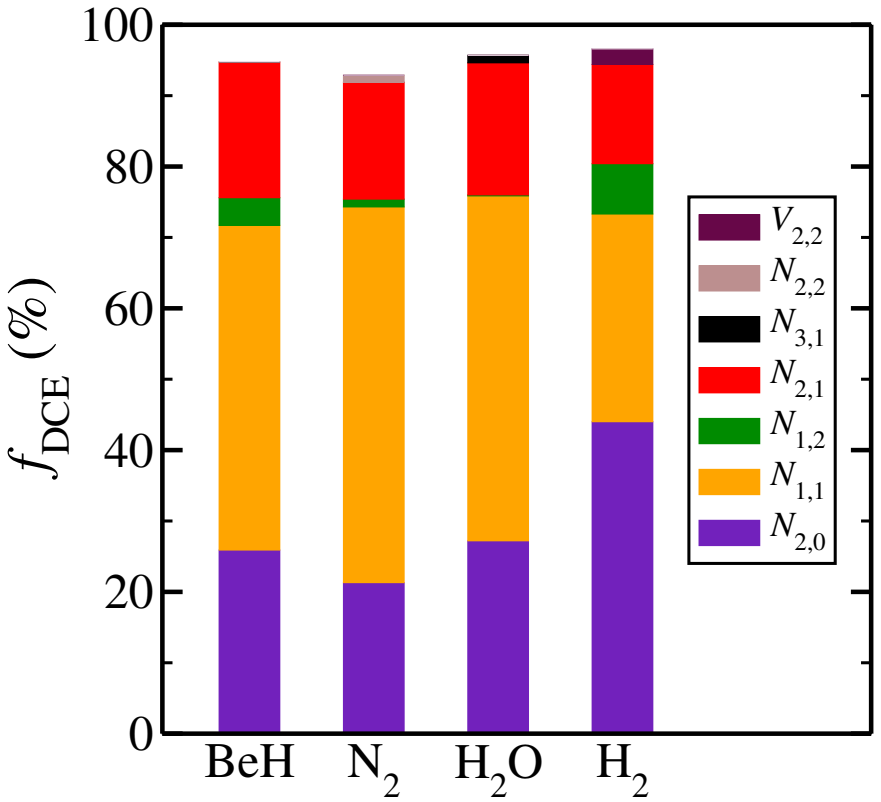
2D HEG

- e–e–e term $N_{3,0}$ (natural powers)
- e–e–e term $C_{3,0}$ (plane waves)

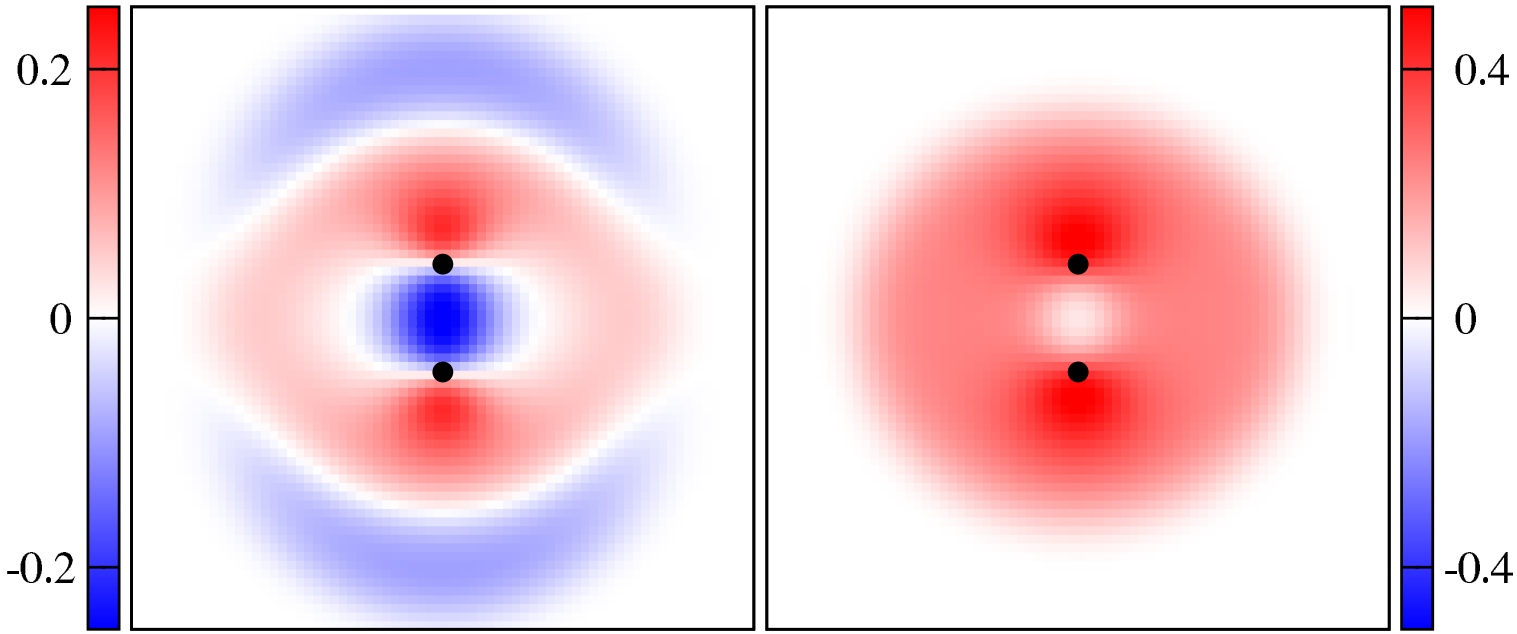


Molecules

- e–n–n term $N_{1,2}$ as orbital correction
- e–e–e–n term $N_{3,1}$



$N_{1,2}$ vs anisotropic e–n term $A^{\text{s.h.}}_{1,1}$ in N_2

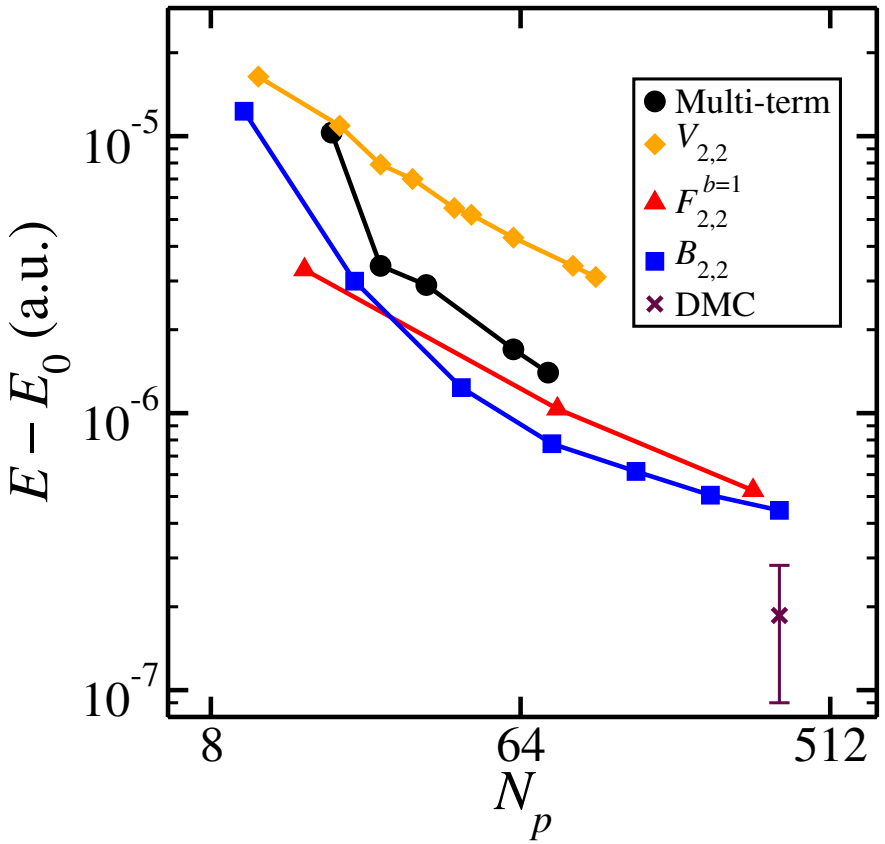


Anisotropic terms in N_2

	E (a.u.)	V (a.u.)	f_{DCE} (%)
HF limit	-108.9929		0
$N_{2,0}$	$-109.102(1)$	5.275(4)	21.3(2)
$+N_{1,1}$	$-109.3739(6)$	3.681(3)	74.3(2)
$+N_{2,1}$	$-109.4441(4)$	1.667(2)	87.9(1)
$+N_{1,2}$	$-109.4644(4)$	1.149(2)	91.9(1)
$+N_{2,2}$	$-109.4697(4)$	1.088(3)	92.9(1)
$+N_{3,0}$	$-109.4702(3)$	1.083(2)	93.0(1)
$N_{2,0}+N_{1,1}+N_{2,1}+A^z_{1,1}$	$-109.4660(3)$	1.116(2)	92.2(1)
$+A^z_{2,1}$	$-109.4707(3)$	1.072(2)	93.1(1)
$+A^{z^2}_{1,1}+A^{z^2}_{2,1}$	$-109.4714(3)$	1.036(4)	93.3(1)
SD DMC	$-109.5060(7)$		100.0(2)

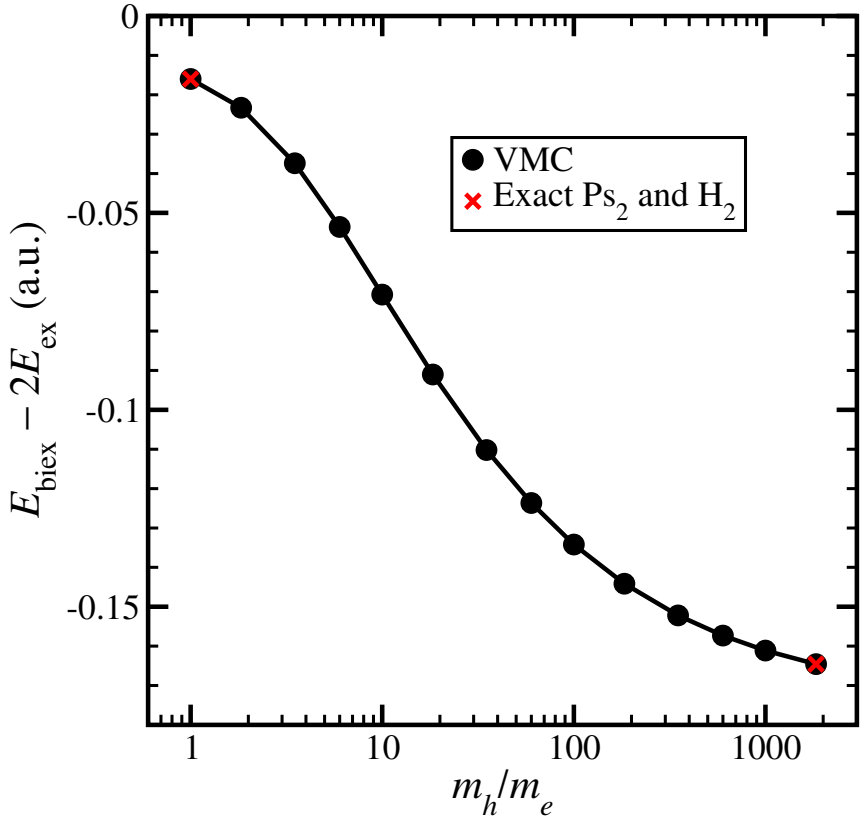
e–e–n–n van der Waals terms in triplet-state H_2

- $F_{2,2}$ term
- Boys-handy $B_{2,2}$ term
- Dipole-dipole $V_{2,2}$ term



From Ps_2 to H_2 without Born-Oppenheimer approx.

- Boys-handy $B_{4,0}$ term
- Error in energy $\sim 10^{-7}$ a.u. digit accuracy in energy, $V \sim 10^{-7} - 10^{-6}$ a.u.



Summary

- A variety of useful terms tested
- Easy extension to new basis functions
- Easy extension to new constraints
- Mission accomplished!
- Next: equivalent framework for backflow

End

End