Explicitly Correlated Second-order Perturbation Theory

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Overview

This lecture introduces the F12 explicitly correlated method for second-order Moller-Plesset many-body perturbation theory. The motivation for the approach is explained and justified and the standard numerical approximations adopted are described.

Review Articles

- Electron correlation: The many-body problem at the heart of chemistry
  Tew, Klopper, Helgaker, J. Comput. Chem. **28**, 1307 (2007)
- Quantitative quantum chemistry
  Helgaker, Klopper, Tew, Mol. Phys. **106**, 2107 (2009)
- The MP2–F12 method in the TURBOMOLE program package
  Bachorz, etal J. Comput. Chem. **32**, 2492 (2011)
- Explicitly Correlated Electrons in Molecules
  Hättig, Klopper, Köhn, Tew, Chem. Rev. **112**, 4 (2012)

MP2 theory (notation and conventions)

First quantised electronic Hamiltonian

$$\hat{H} = \sum_{i}^{n} h_i + \sum_{i<j}^{n} \frac{1}{r_{ij}} \qquad h_i = -\tfrac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}}$$

Second quantised electronic Hamiltonian

$$\hat{H} = \sum_{pq} h_p^q a_q^\dagger a_p + \tfrac{1}{2} \sum_{pqrs} g_{rs}^{pq} a_p^\dagger a_q^\dagger a_s a_r$$

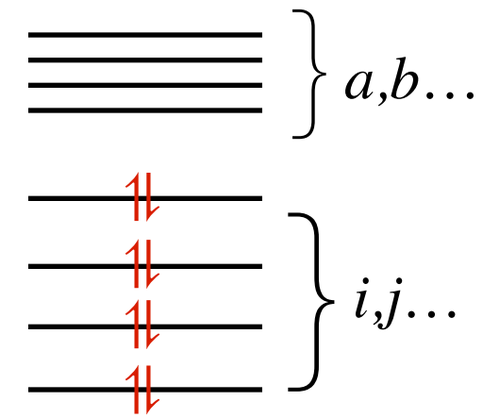
$$h_p^q = \langle q|h|p\rangle = \int \phi_q^*(1) h_1 \phi_p(1)\, d1$$

$$g_{rs}^{pq} = \langle pq|r_{12}^{-1}|rs\rangle = \int \phi_p^*(1)\phi_q^*(2) r_{12}^{-1} \phi_r(1)\phi_s(2)\, d1 d2$$

$$\hbar = 4\pi\epsilon_0 = m_e = e = 1$$

MP2 theory (notation and conventions)

The 0th order Hamiltonian is the Fock operator



$$\hat{H}^0 = \sum_{pq} f_p^q a_q^\dagger a_p \qquad f_p^q = \delta_p^q \epsilon_p$$

$$|0\rangle = \frac{1}{\sqrt{n!}} \hat{A} |\phi_1(1)\phi_2(2)\ldots\phi_n(n)\rangle$$

The perturbation expansion

$$(\hat{H}^0 + \lambda \hat{H}^1)(|0\rangle + \lambda|1\rangle + \cdots) = (E^0 + E^1 + \cdots)(|0\rangle + \lambda|1\rangle + \cdots)$$

$$\hat{H}^0|0\rangle = E^0|0\rangle \qquad E_{\mathrm{HF}} = E^0 + E^1$$

$$E^1 = \langle 0|\hat{H}^1|0\rangle \qquad E_{\mathrm{corr}} \approx E^2$$

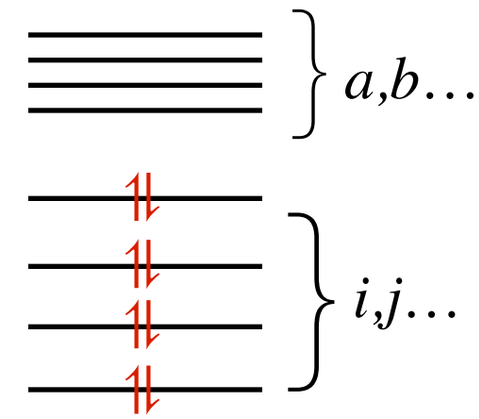
$$E^2 = \langle 0|\hat{H}^1|1\rangle$$

HF energy is effective energy of best independent particle model

The second-order energy arises from electron correlation

MP2 theory (notation and conventions)

The 0th order Hamiltonian is the Fock operator



$$\hat{H}^0 = \sum_{pq} f_p^q a_q^\dagger a_p \qquad f_p^q = \delta_p^q \epsilon_p$$

$$|0\rangle = \frac{1}{\sqrt{n!}} \hat{A} |\phi_1(1)\phi_2(2)\ldots\phi_n(n)\rangle$$

First order wavefunction: $(\hat{H}^0 - E^0)|1\rangle = (E^1 - \hat{H}^1)|0\rangle$

$$|1\rangle = \sum_{ia} T_i^a a_a^\dagger a_i |0\rangle + \frac{1}{4} \sum_{ijab} T_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |0\rangle + \ldots$$

Only double excitations (pair correlations) contribute to E^2

Each pair equation is independent of the others

$$T_{ij}^{ab} = -\frac{g_{ij}^{ab}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \qquad E^2 = -\frac{1}{4} \sum_{ijab} \frac{g_{ij}^{ab}(2g_{ij}^{ab} - g_{ij}^{ba})}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$

Standard basis set expansion

1st order wavefunction $$|1\rangle = \frac{1}{4}\sum_{ijab} T_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |0\rangle$$

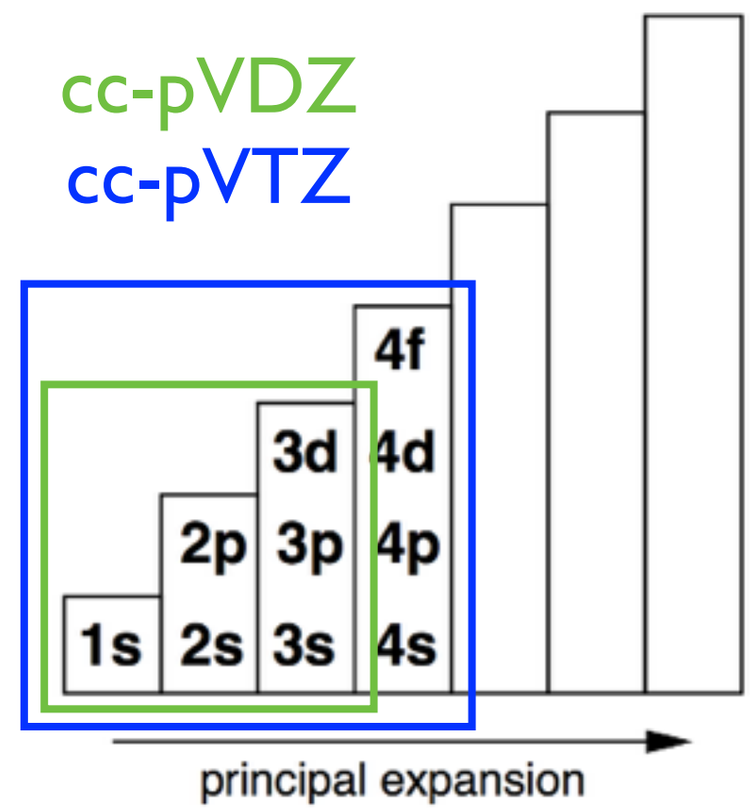
Pair functions (1stQ) $$|u_{ij}\rangle = \frac{1}{2}\sum_{ab} t_{ab}^{ij} |ab\rangle$$

The one-particle (Fock) states are expanded in terms of atomic functions χ_κ (LCAO)

$$\phi_a = \sum_\kappa C_{\kappa,a}\chi_\kappa$$

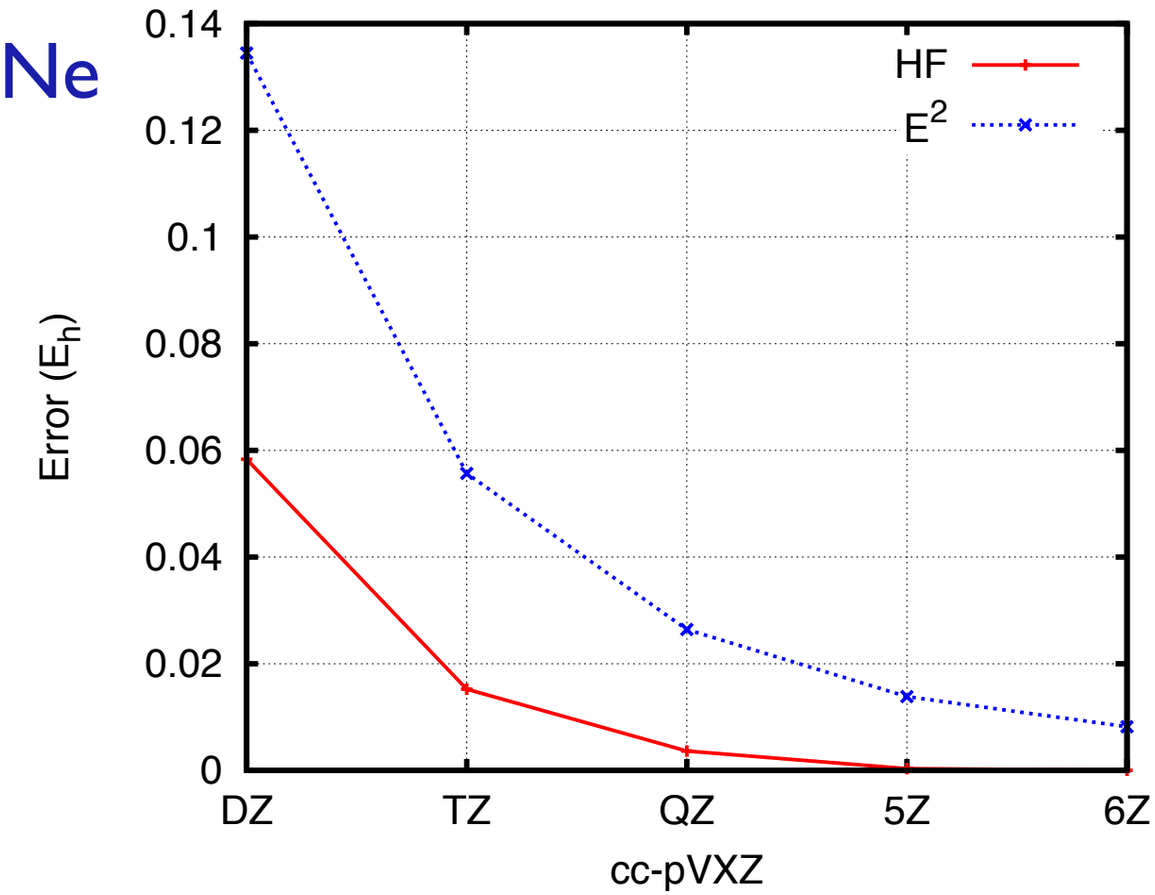
$$\chi_\kappa(r) = H_\kappa(r-A)e^{-\alpha_\kappa|r-A|^2}$$

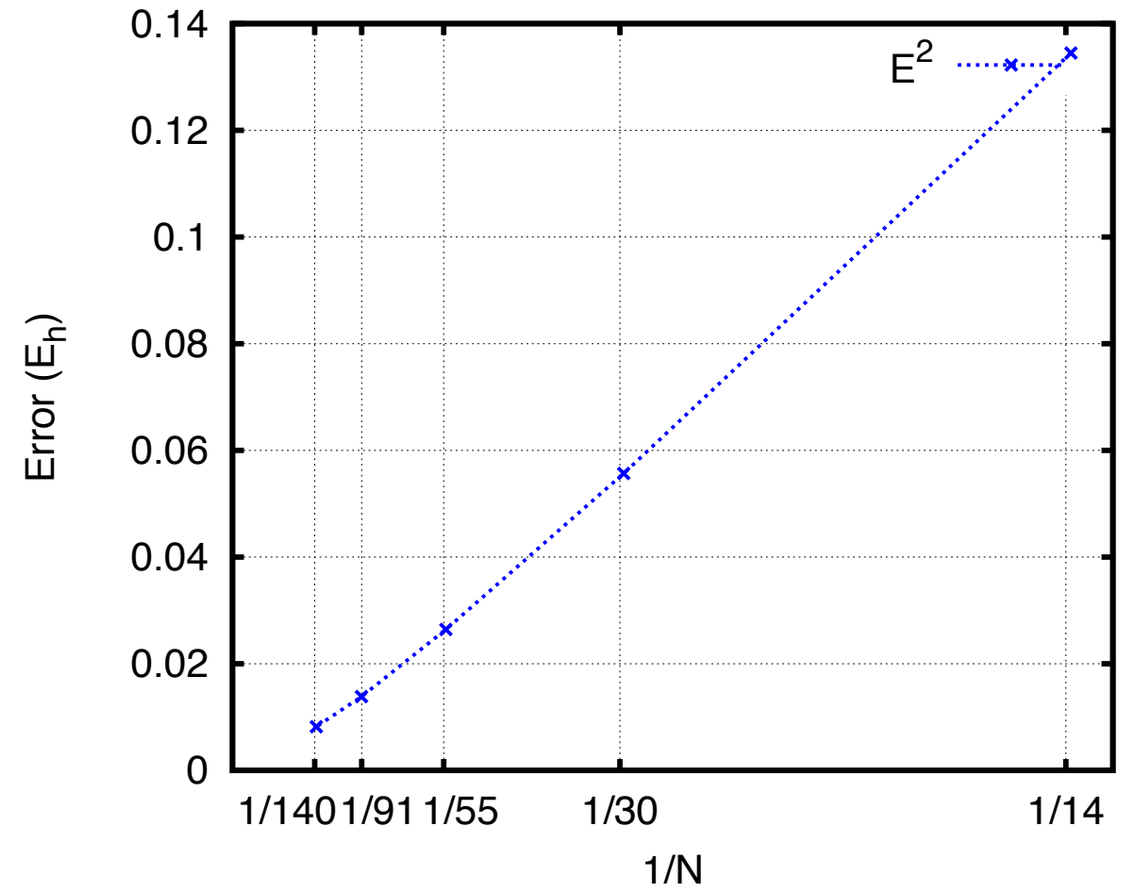
$$H_\kappa(r) = x^l y^m z^n$$



MP2 basis set convergence

Ne





Cost of building integrals scales (at least) as N^4

Reducing error by a factor of 10 increases cost 10000 times

cc-pVDZ: 3s+2p+1d = 14
cc-pVTZ: 4s+3p+2d+1f = 30

Coulomb singularities and wavefunction cusps

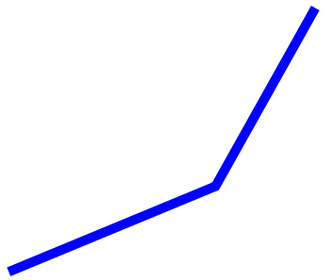
The electronic Schrödinger equation has coulomb singularities whenever charged particles coalesce.

e.g. helium

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

To satisfy $\hat{H}\Psi = E\Psi$ infinities in the potential must be exactly cancelled by infinities in the kinetic energy.

Infinities in the kinetic energy arise when there is a derivative discontinuity in Ψ:



Coulomb singularities and wavefunction cusps

Nuclear cusps are familiar

e.g. hydrogen

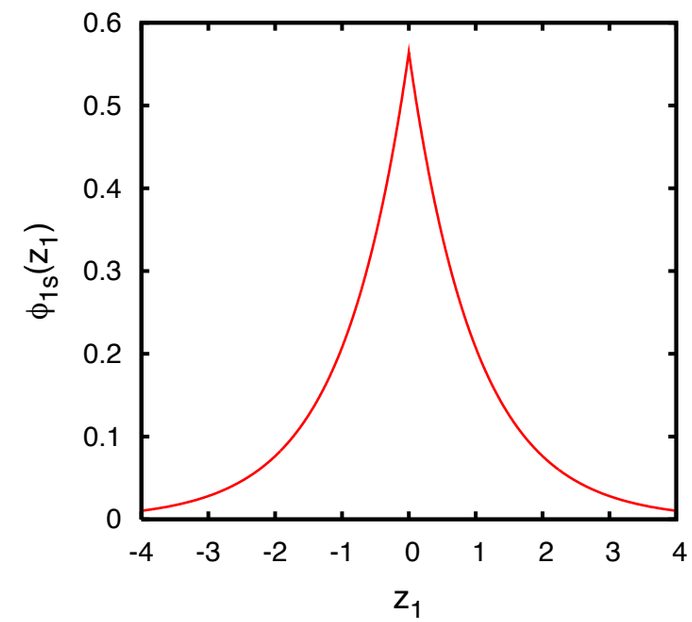
1s

$$\varphi_{1s}(\mathbf{r}_1) = \pi^{-1/2}\exp(-r_1)$$

$$\varphi_{1s}(0,0,z_1) \propto (1 - |z_1| + \cdots)$$

discontinuity in the first derivative

$$\left.\frac{\widetilde{\partial\psi}}{\partial r_{1A}}\right|_{r_{1A}=0} = -Z_A\psi(r_{1A}=0)$$



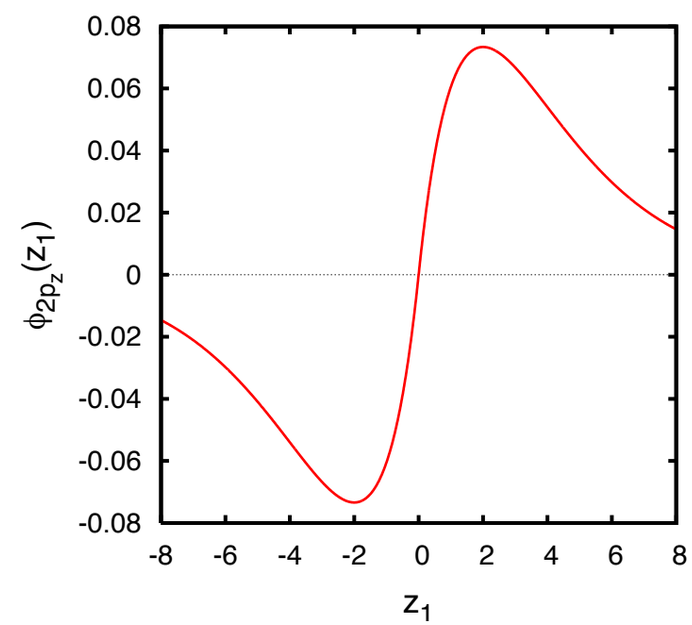
2p (wave function is zero at coalescence point)

$$\varphi_{2p_z}(\mathbf{r}_1) = (32/\pi)^{1/2} z_1 \exp(-r_1/2)$$

$$\varphi_{2p_z}(0,0,z_1) \propto z_1(1 - |z_1|/2 + \cdots)$$

discontinuity in the second derivative

$$\left.\frac{\widetilde{\partial^2\psi}}{\partial r_{1A}^2}\right|_{r_{1A}=0} = -Z_A\left.\frac{\widetilde{\partial\psi}}{\partial r_{1A}}\right|_{r_{1A}=0}$$



Coulomb singularities and wavefunction cusps

Electron cusps are analogous

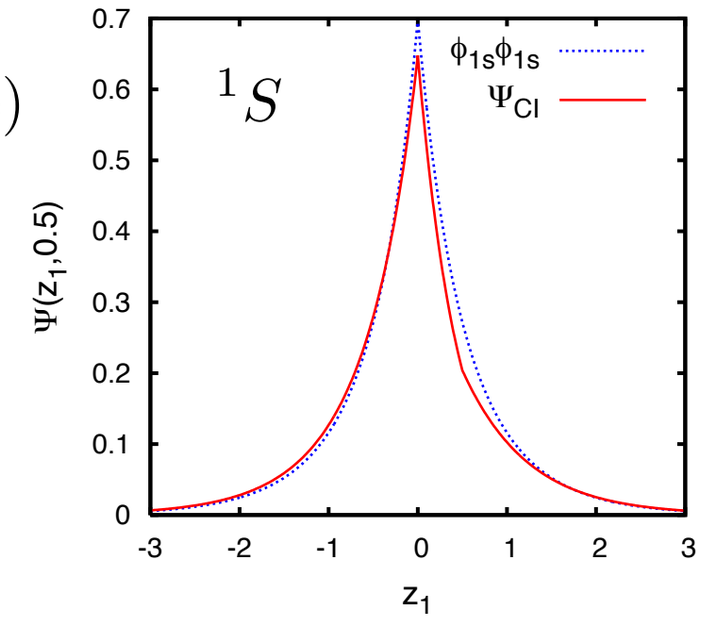
e.g. helium

Single pairs (s-waves)

$$\left.\widetilde{\frac{\partial\psi}{\partial r_{12}}}\right|_{r_{12}=0} = \frac{1}{2}\psi(r_{12}=0)$$

$$\psi = \psi(r_{12}=0)(1+\tfrac{1}{2}r_{12}) + \mathcal{O}(r_{12}^2)$$

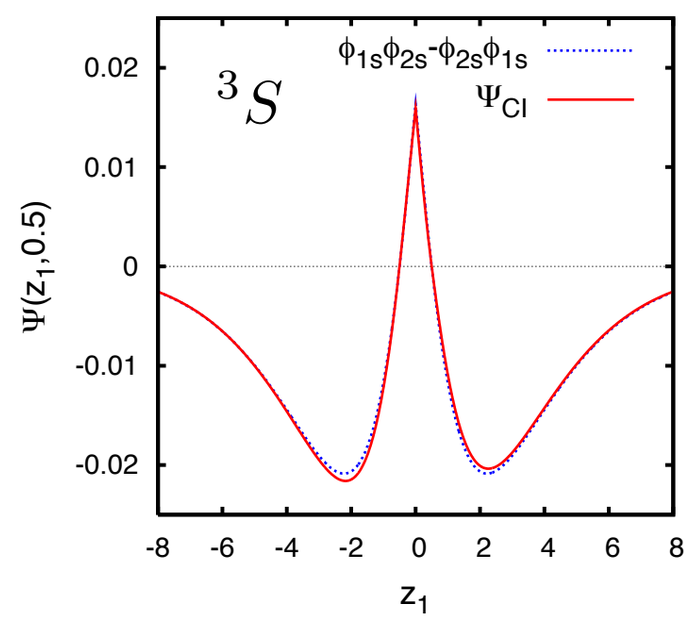
$\psi(z_1, 0.5)$



Triplet pairs (p-waves)

$$\left.\widetilde{\frac{\partial^2\psi}{\partial r_{12}^2}}\right|_{r_{12}=0} = \frac{1}{2}\left.\widetilde{\frac{\partial\psi}{\partial r_{12}}}\right|_{r_{12}=0}$$

$$\psi = \left.\frac{\partial\psi}{\partial\mathbf{r}_{12}}\right|_{r_{12}=0}\cdot\mathbf{r}_{12}(1+\tfrac{1}{4}r_{12}) + \mathcal{O}(r_{12}^3)$$



First-order coalescence conditions

The first order wave equation $(\hat{H}^0 - E^0)|1\rangle = (\hat{H}^1 - E^1)|0\rangle$

$$\left(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j\right)|u_{ij}\rangle = \left(r_{12}^{-1} - E^1\right)|ij\rangle$$

Expressed in terms of $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ $\mathbf{s} = (\mathbf{r}_1 + \mathbf{r}_2)/2$

$$\left(-\nabla_r^2 + \mathcal{O}(r^0)\right)|u_{ij}\rangle + \left(r^{-1} + \mathcal{O}(r^0)\right)|ij\rangle = 0$$

Singlet pairs:

$|ij\rangle = \phi_i\phi_j\left(\alpha\beta - \beta\alpha\right)/\sqrt{2}$ $|u_{ij}\rangle = \frac{1}{2}r_{12}|ij\rangle + \mathcal{O}(r_{12}^2)$

Triplet pairs:

$|ij\rangle = \left(\phi_i\phi_j - \phi_j\phi_i\right)\alpha\alpha/\sqrt{2}$ $|u_{ij}\rangle = \frac{1}{4}r_{12}|ij\rangle + \mathcal{O}(r_{12}^3)$

First-order coalescence conditions

The first order wave equation $(\hat{H}^0 - E^0)|1\rangle = (\hat{H}^1 - E^1)|0\rangle$

$$\left(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j\right)|u_{ij}\rangle = \left(r_{12}^{-1} - E^1\right)|ij\rangle$$

Expressed in terms of $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ $\mathbf{s} = (\mathbf{r}_1 + \mathbf{r}_2)/2$

$$\left(-\nabla_r^2 + \mathcal{O}(r^0)\right)|u_{ij}\rangle + \left(r^{-1} + \mathcal{O}(r^0)\right)|ij\rangle = 0$$

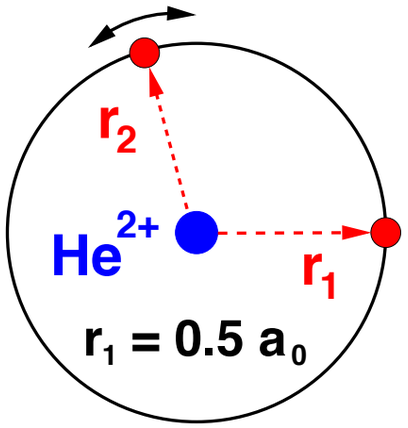
Spin orbit: $|u_{ij}\rangle = \frac{3}{8}r_{12}|ij\rangle + \frac{1}{8}r_{12}|ji\rangle + \mathcal{O}(r_{12}^2)$

In the limit of a complete one-partilce basis, in 2ndQ this is

$$|1\rangle = \frac{1}{4}\sum_{ijab} R_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |0\rangle + |1'\rangle$$

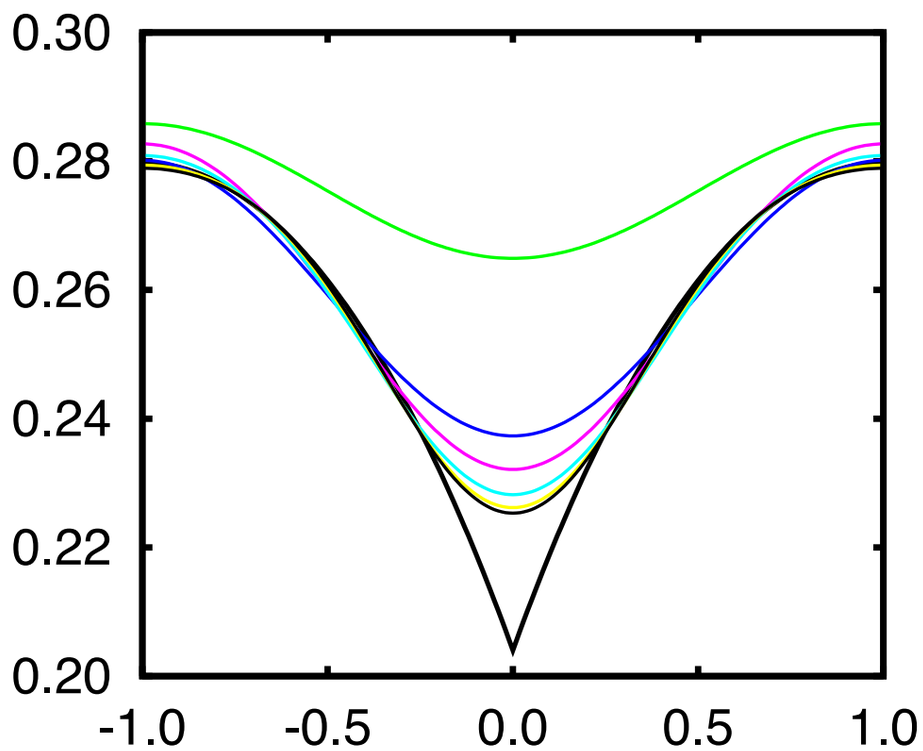
$$R_{ij}^{ab} = \frac{3}{8}\langle ab|r_{12}|ij\rangle + \frac{1}{8}\langle ab|r_{12}|ji\rangle$$

Basis set convergence

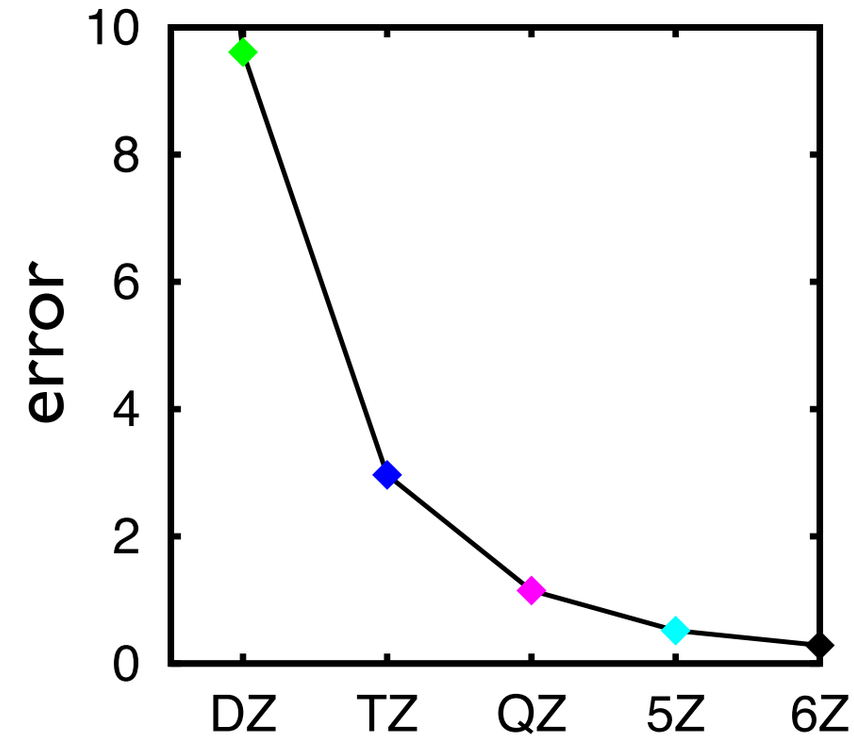


The correlation hole has a cusp at $r_{12} = 0$ arising from the Coulomb singularity

$$\Psi = \Psi_0(1 + \tfrac{1}{2}r_{12}) + \mathcal{O}(r_{12}^2)$$



X = D, T, Q, 5, 6



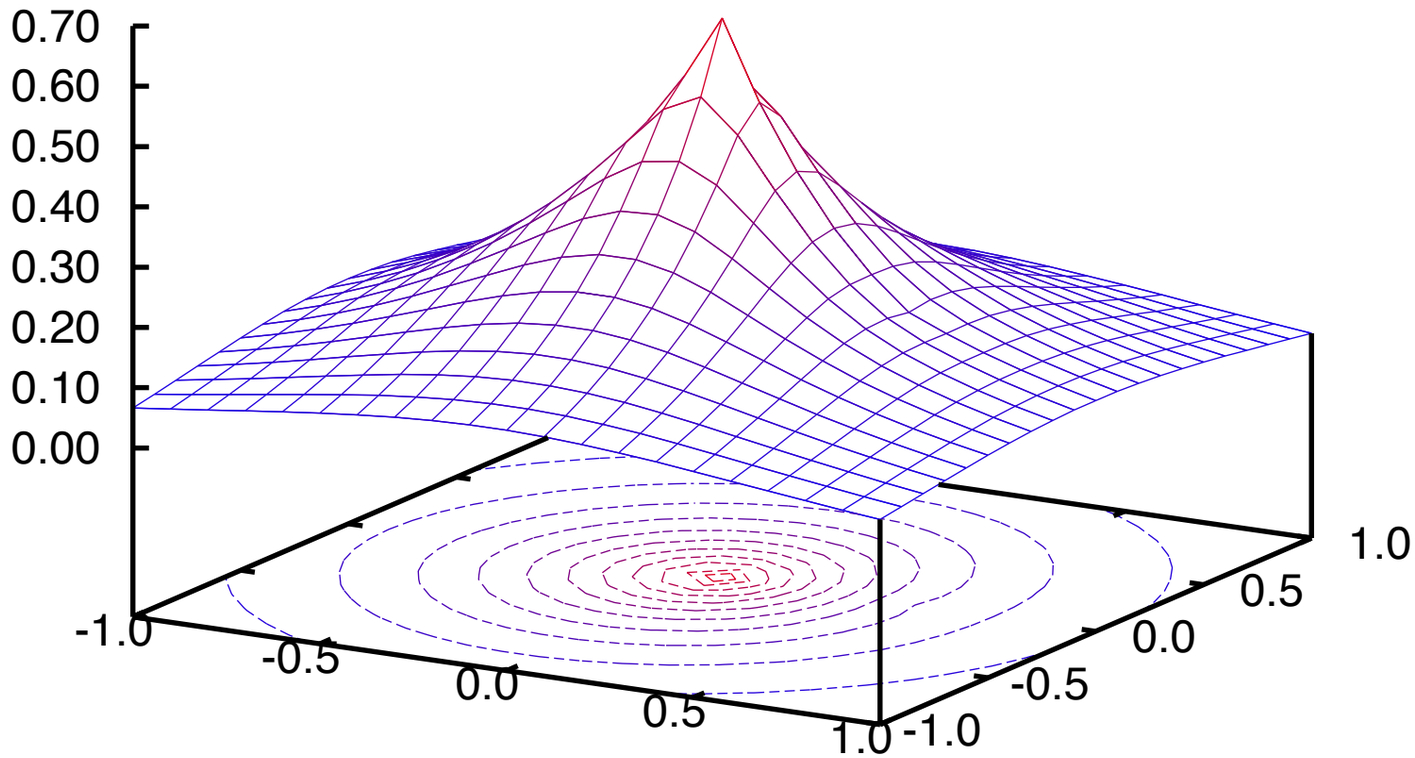
cc-pVXZ

Sharp features away from the nucleus are not well represented using products of smooth, atom-centred AOs

Visualising He wavefunctions

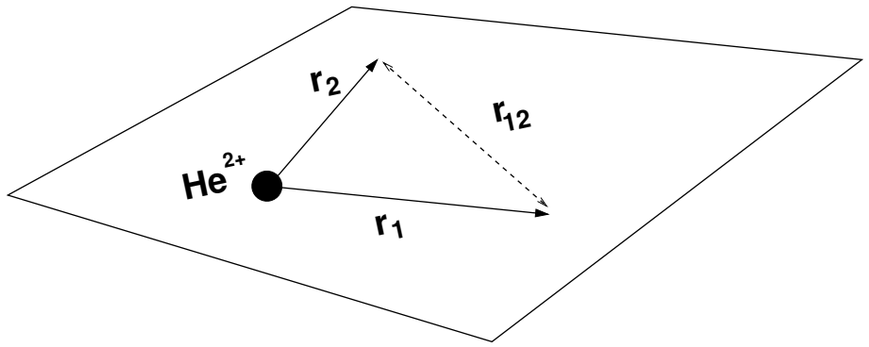
The positions of the three particles defines a plane.

Depict the wavefunction as a function of where electron 2 lies the plane, keeping electron 1 at some distance from the nucleus.



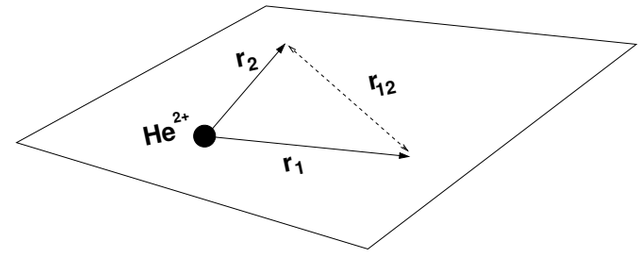
$$\Psi = |1s1s\rangle$$

$$\mathbf{r}_1 = (0.5, 0, 0)$$

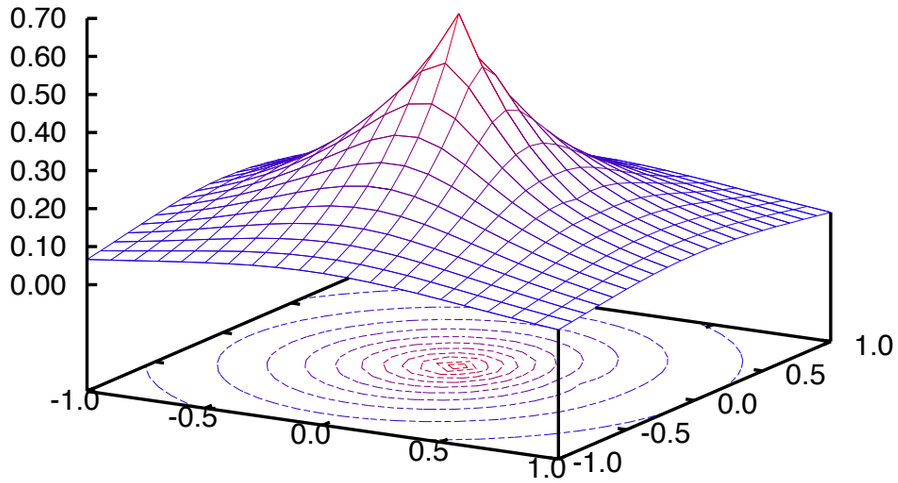


For the HF wavefunction this is simply the $1s$ orbital for electron 2 multiplied by $\phi_{1s}(r = 0.5)$

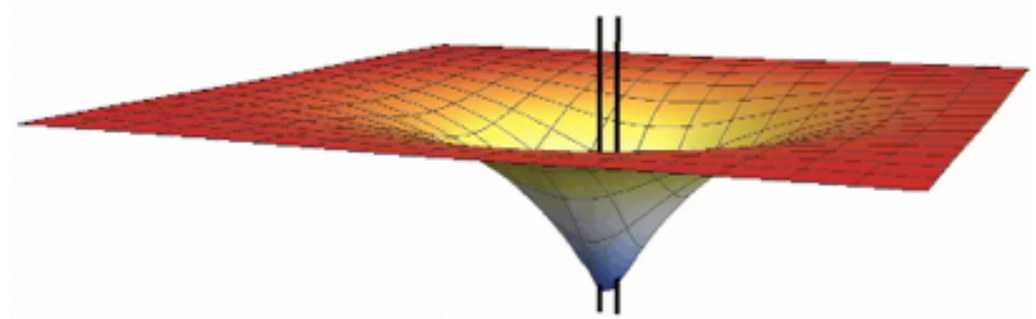
Helium correlation holes



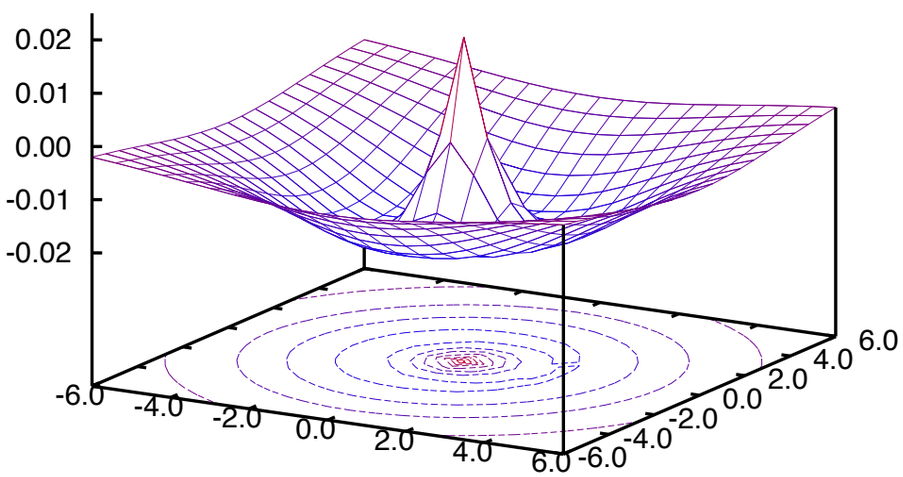
$1s^2(\alpha\beta - \beta\alpha)$



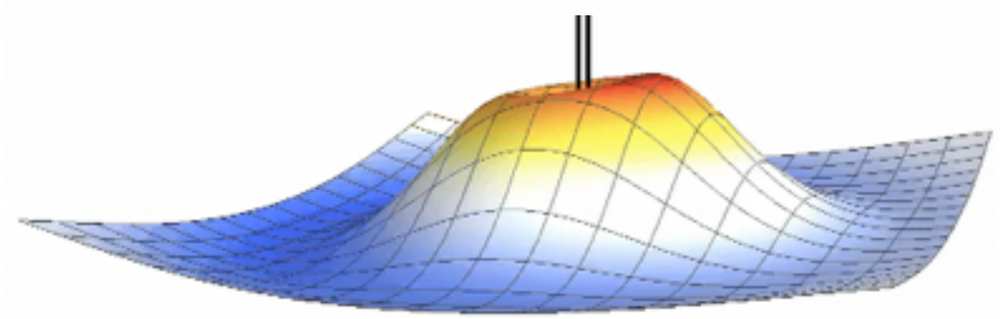
$\Psi - \Psi_{\mathrm{HF}}$



$(1s2s - 2s1s)\alpha\alpha$



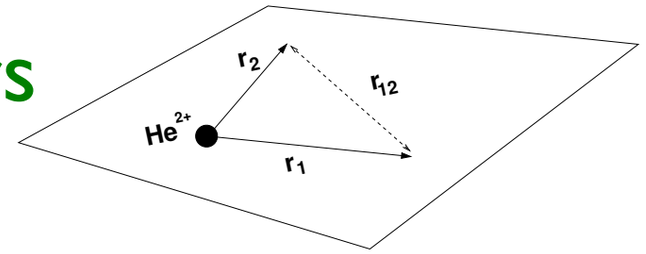
$\Psi - \Psi_{\mathrm{HF}}$



Derivative discontinuities at Coulomb singularities

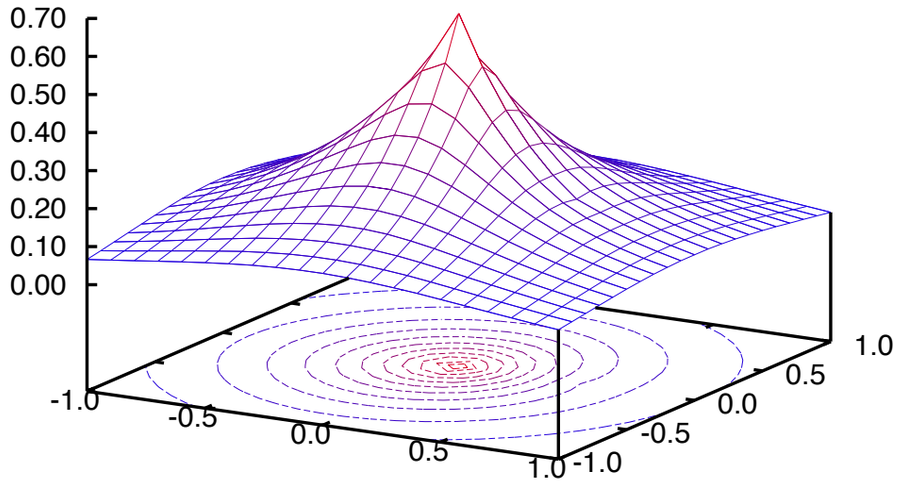
$$\left.\frac{\partial \Psi^{(0)}}{\partial r_{12}}\right|_{r_{12}=0} = \frac{1}{2}\Psi^{(0)}\Big|_{r_{12}=0} \qquad \left.\frac{\widetilde{\partial^2 \Psi}^{(1)}}{\partial r_{12}^2}\right|_{r_{12}=0} = \frac{1}{2}\left.\frac{\widetilde{\partial \Psi}^{(1)}}{\partial r_{12}}\right|_{r_{12}=0}$$

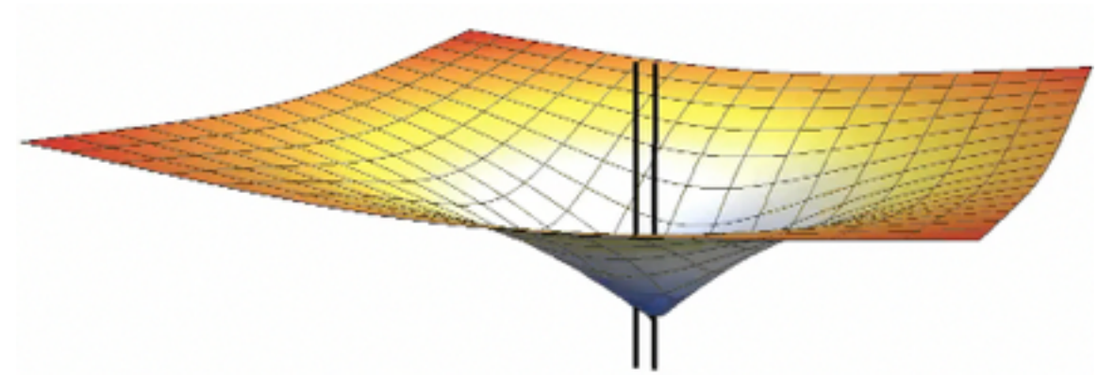
Helium correlation factors



$1s^2(\alpha\beta - \beta\alpha)$

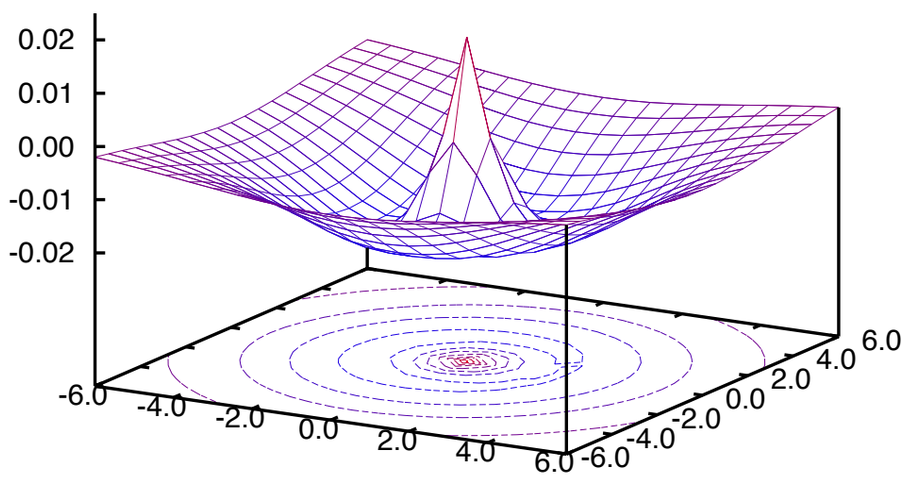
$$J = (\Psi - \Psi_{\mathrm{HF}})/\Psi_{\mathrm{HF}}$$

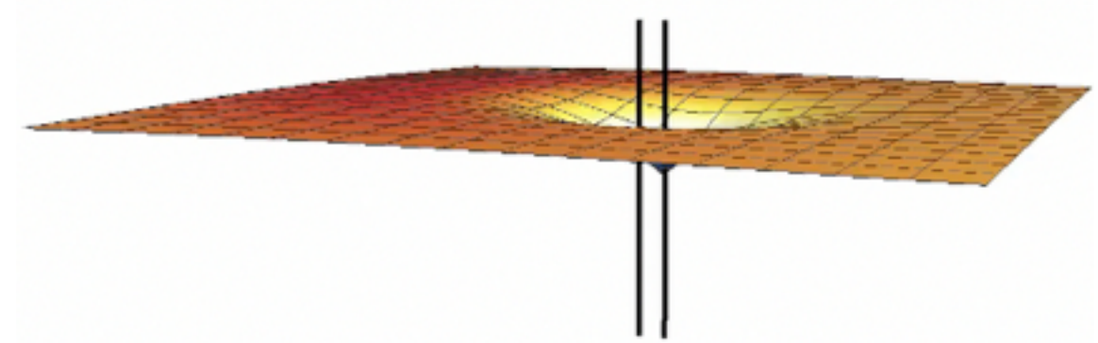




$(1s2s - 2s1s)\alpha\alpha$

$$J = (\Psi - \Psi_{\mathrm{HF}})/\Psi_{\mathrm{HF}}$$





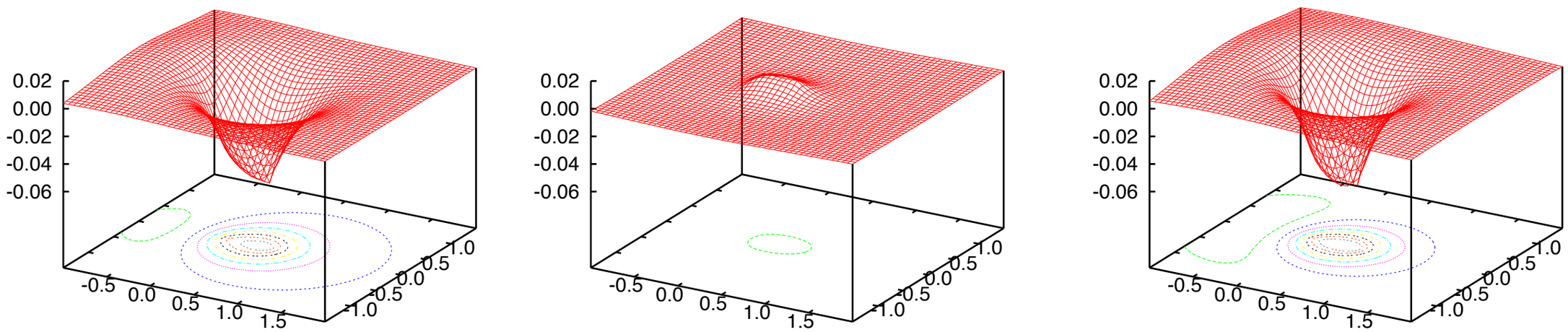
The correlation (Jastrow) factor : $\Psi = (1 + J)\Psi_{\mathrm{HF}}$

Almost constant in size and remarkably isotropic in r_{12}

Kutzelnigg-Tenno Ansatz

In F12 theory the pair correlation function is written as

$$|u_{ij}\rangle = \sum_{a<b} t_{ab}^{ij} |\phi_a \phi_b\rangle + \hat{Q}_{12} \hat{S}_{12} f_{12} |\phi_i \phi_j\rangle$$



The geminal $-\frac{1}{\gamma} e^{-\gamma r_{12}} S_{12} |\phi_i \phi_j\rangle$ is an excellent model for the correlation function for orbital pair $|\phi_i \phi_j\rangle$

r12-Dependent terms in the wave function as closed sums of partial wave amplitudes for large l. W. Kutzelnigg Theor. Chimica Acta 68 445 (1985)

Kutzelnigg-Tenno Ansatz

In F12 theory the pair correlation function is written as

$$|u_{ij}\rangle = \sum_{a<b} t_{ab}^{ij} |\phi_a \phi_b\rangle + \hat{Q}_{12} \hat{S}_{12} f_{12} |\phi_i \phi_j\rangle$$

F12 geminal function

In 2ndQ the first-order wavefunction is written as

$$|1\rangle = \frac{1}{4} \sum_{ijab} T_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i |0\rangle + \frac{1}{4} \sum_{ij\alpha\beta} R_{ij}^{\alpha\beta} a_\alpha^\dagger a_\beta^\dagger a_j a_i |0\rangle$$

$$R_{ij}^{\alpha\beta} = \tfrac{3}{8} \langle \alpha\beta | \hat{Q}_{12} f_{12} | ij\rangle + \tfrac{1}{8} \langle \alpha\beta | \hat{Q}_{12} f_{12} | ji\rangle$$

$$f_{12} = \tfrac{1}{\gamma}(1 - e^{-\gamma r_{12}})$$

S_{12} is the rational generator, or spin-flip operator

Q_{12} is the strong orthogonality projector

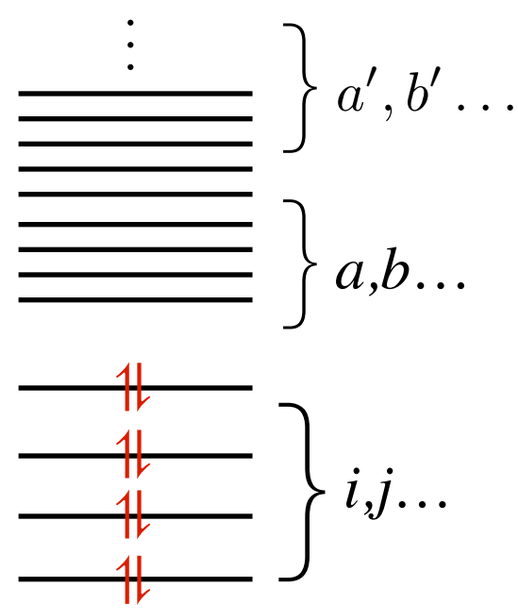
γ is a lengthscale parameter, usually set to $1/a_0$.

Strong Orthogonality Projector

The first-order wavefunction only contains contributions from double excitations. Q_{12} projects out all contributions from the F12 geminal function that are outside this double space.

$$
\begin{aligned}
Q_{12} &= (1 - O_1)(1 - O_2)(1 - V_1 V_2) \\
&= 1 - P_1 P_2 - O_1 V_2' - V_1' O_2
\end{aligned}
$$

	j	*b*	*b'*
i	HF	S	S'
a	S	D	D'
a'	S'	D'	D'



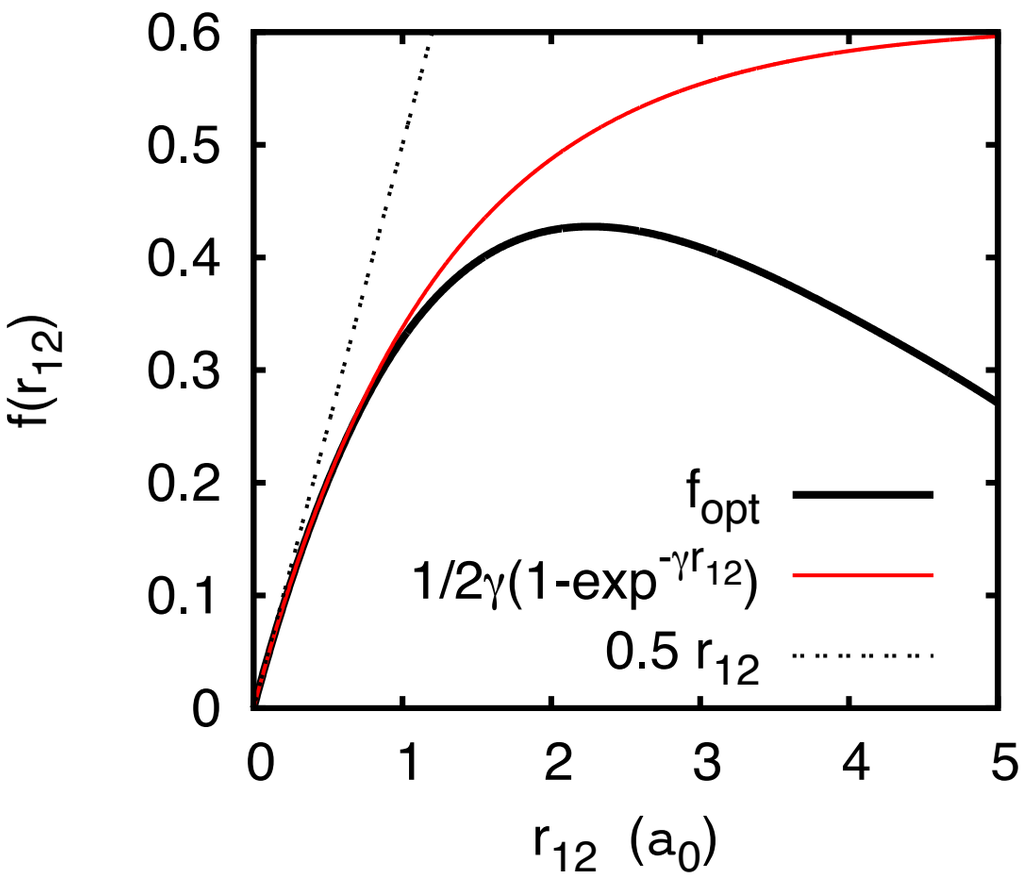
$$
\begin{aligned}
V' &= |a'\rangle\langle a'| \\
V &= |a\rangle\langle a| \\
O &= |i\rangle\langle i| \\
P &= O + V
\end{aligned}
$$

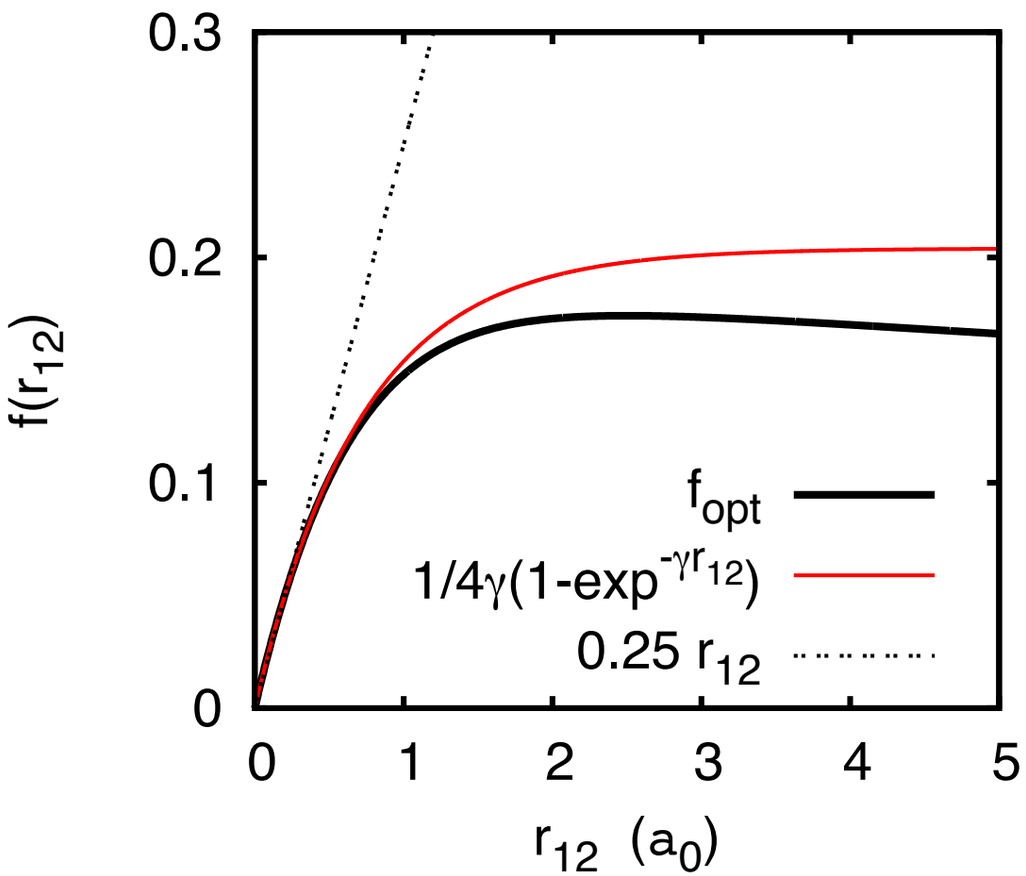
$$
f_{12}|ij\rangle = \sum_{\alpha\beta} F_{ij}^{\mu\nu} |\mu\nu\rangle
$$

Optimum correlation factor

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (1 + f(r_{12}))\Psi_{\mathrm{HF}}(\mathbf{r}_1, \mathbf{r}_2) + \Psi'(\mathbf{r}_1, \mathbf{r}_2)$$

Use Hylleraas wave function and project to find f





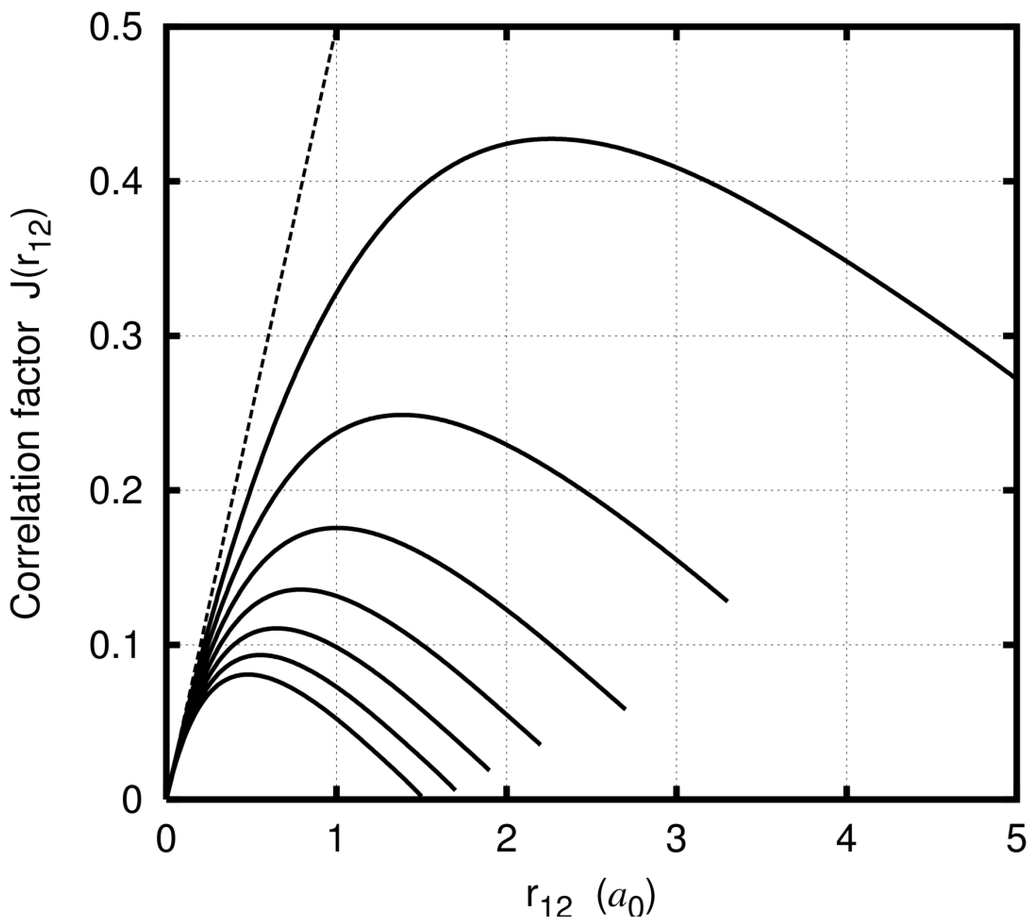
singlet $$\left.\frac{\partial \Psi^{(0)}}{\partial r_{12}}\right|_{r_{12}=0} = \left.\frac{1}{2}\Psi^{(0)}\right|_{r_{12}=0}$$

triplet $$\left.\frac{\widetilde{\partial^2 \Psi}^{(1)}}{\partial r_{12}^2}\right|_{r_{12}=0} = \left.\frac{1}{2}\frac{\widetilde{\partial \Psi}^{(1)}}{\partial r_{12}}\right|_{r_{12}=0}$$

Lengthscale of the correlation hole

The optimum correlation factor for 2-electron cations Li^{+} … O^{6+}

Z	2	3	4	5	6	7	8
$\gamma(a_0^{-1})$	0.81	1.55	2.27	2.99	3.70	4.42	5.12
a(Z-b)	0.83	1.54	2.26	2.98	3.70	4.42	5.13



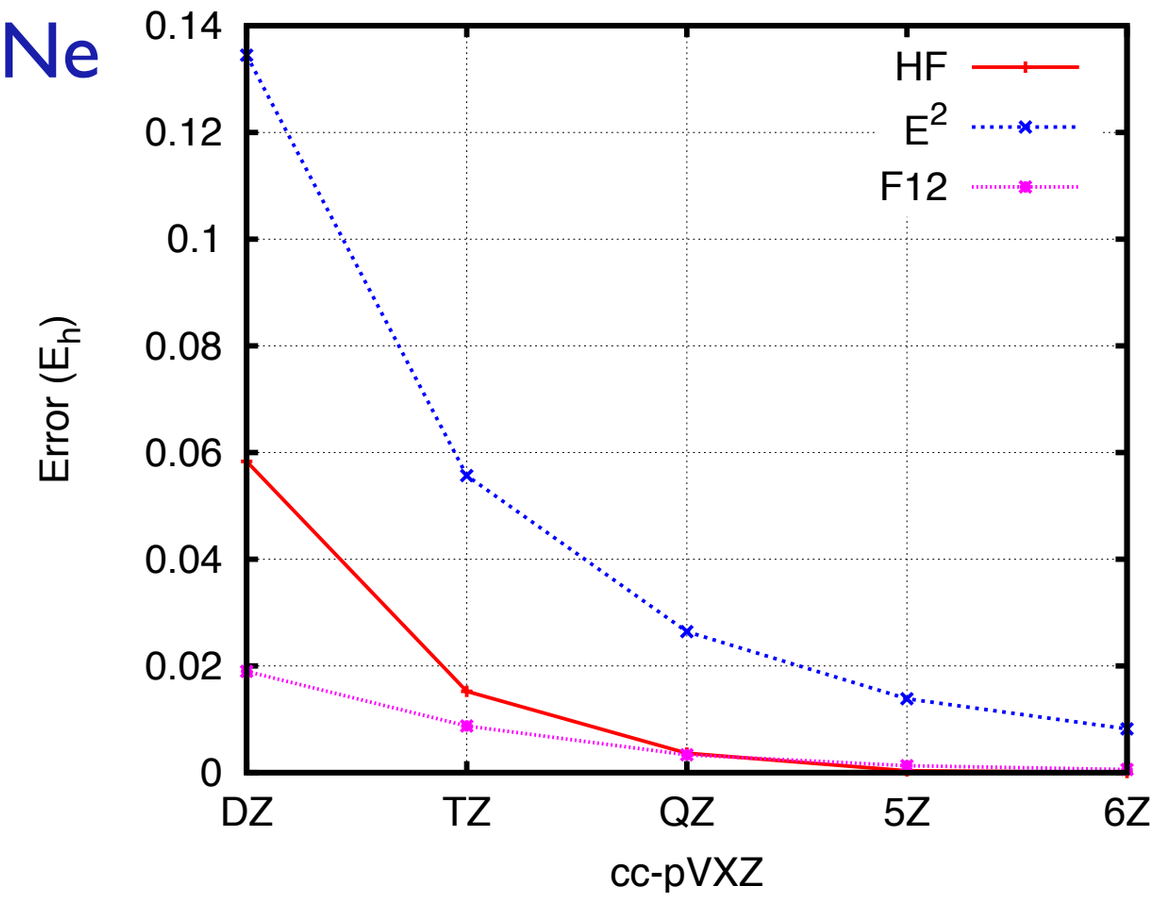
$$f(r_{12}) = \frac{1}{2\gamma}(1 - e^{-\gamma r_{12}})$$

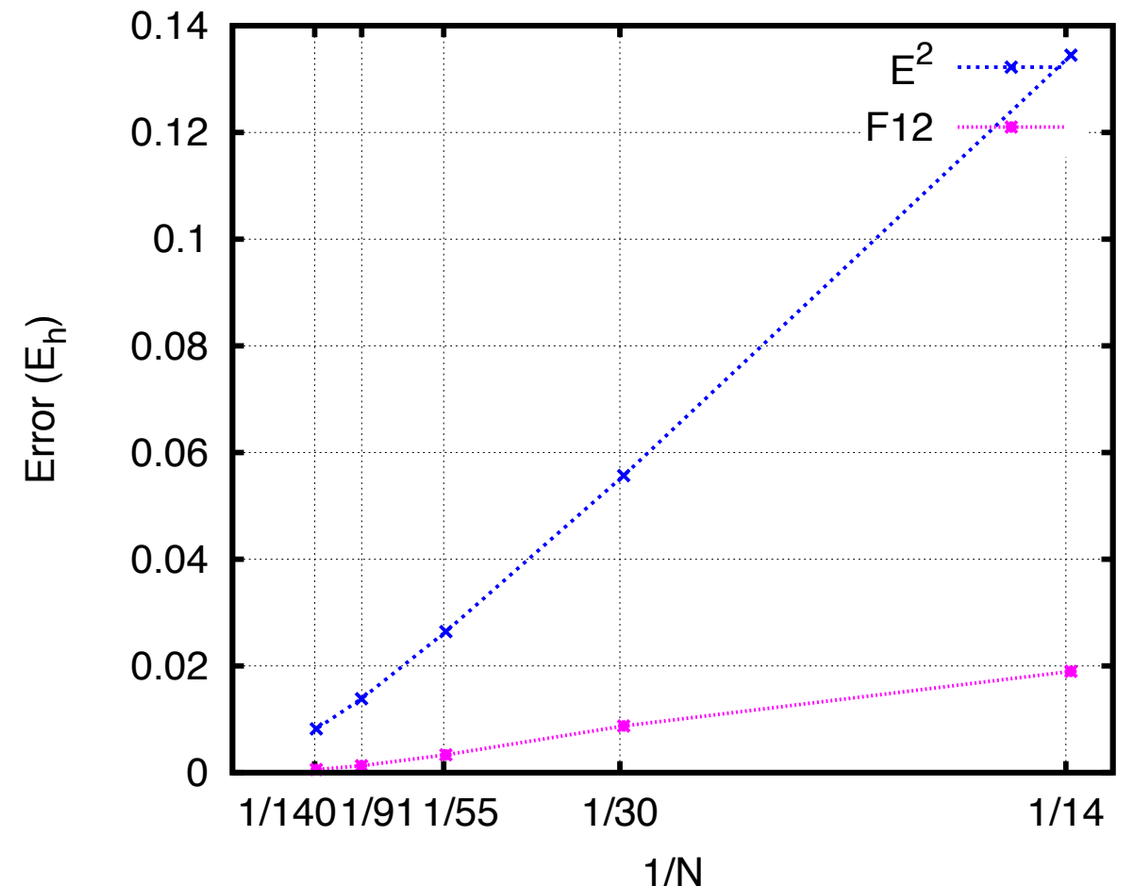
$$\gamma \approx a(Z - b) \qquad a = 0.718 \qquad b = 0.848$$

Valance	0.8-1.4
Core-Val.	1.8-2.6
Core	1.8-2.6

MP2-F12 basis set convergence

Ne





Correlation energy from MP2-F12/cc-pVDZ more accurate than from MP2/cc-pVQZ

$$|u_{ij}\rangle = \sum_{a<b} t_{ab}^{ij} |\phi_a \phi_b\rangle + \hat{Q}_{12} \hat{S}_{12} f_{12} |\phi_i \phi_j\rangle$$

General MP2-F12 equations

In the general case, coefficients for both the orbital product and geminal basis functions are optimised

$$|u_{ij}\rangle = \frac{1}{2}\sum_{ab} t_{ab}^{ij}|ab\rangle + \frac{1}{2}\sum_{xy} c_{xy}^{ij} Q_{12}S_{12}f_{12}|xy\rangle$$

$$|\bar{ij}\rangle = 2|ij\rangle - |ji\rangle$$

$$E_{ij}^2 = \langle \bar{ij}|r_{12}^{-1}|u_{ij}\rangle$$

$$0 = \langle cd|(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j)|u_{ij}\rangle + \langle cd|r_{12}^{-1}|ij\rangle$$

$$0 = \langle vw|f_{12}S_{12}Q_{12}(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j)|u_{ij}\rangle + \langle vw|f_{12}S_{12}Q_{12}r_{12}^{-1}|ij\rangle$$

Equivalent to minimising the Hylleraas functional

$$H_{ij}^2 = \langle \bar{u}_{ij}|(\hat{F}_1 + \hat{F}_2 - \epsilon_i - \epsilon_j)|u_{ij}\rangle + 2\langle \bar{ij}|r_{12}^{-1}|u_{ij}\rangle$$

If the F12 coefficients are fixed as $c_{xy}^{ij} = \delta_x^i\delta_y^j - \delta_x^j\delta_y^i$ to satisfy the coalescence conditions (recommended), the energy is the minimum of the Hylleraas functional w.r.t the t_{ab}^{ij} coefficients.

General MP2-F12 equations

$$E^2_{ij} = \frac{1}{2}\sum_{ab} t^{ij}_{ab}(2g^{ab}_{ij} - g^{ba}_{ij}) + \frac{1}{2}\sum_{xy} c^{ij}_{xy}(2V^{xy}_{ij} - V^{yx}_{ij})$$

$$\begin{pmatrix} \delta^{cd}_{ab}\varepsilon^{ij}_{ab} & C^{vw}_{ab} \\ C^{cd}_{xy} & B^{vw}_{xy} - X^{vw}_{xy}\varepsilon^{ij} \end{pmatrix} \begin{pmatrix} t^{ij}_{cd} \\ c^{ij}_{vw} \end{pmatrix} = - \begin{pmatrix} g^{ij}_{ab} \\ V^{ij}_{xy} \end{pmatrix}$$

$$\begin{aligned}
B^{vw}_{xy} &= \langle xy|f_{12}\hat{\mathcal{S}}_{xy}\hat{Q}_{12}(\hat{F}^0_1 + \hat{F}^0_2)\hat{Q}_{12}\hat{\mathcal{S}}_{vw}f_{12}|vw\rangle \\
C^{vw}_{ab} &= \langle ab|(\hat{F}^0_1 + \hat{F}^0_2)\hat{Q}_{12}\hat{\mathcal{S}}_{vw}f_{12}|vw\rangle \\
X^{vw}_{xy} &= \langle xy|f_{12}\hat{\mathcal{S}}_{xy}\hat{Q}_{12}\hat{\mathcal{S}}_{vw}f_{12}|vw\rangle \\
V^{ij}_{xy} &= \langle xy|f_{12}\hat{\mathcal{S}}_{xy}\hat{Q}_{12}r^{-1}_{12}|ij\rangle \\
g^{ij}_{ab} &= \langle ab|r^{-1}_{12}|ij\rangle
\end{aligned}$$

Need to evaluate the F12 intermediates

Many-electron integrals: The RI approximation

The F12 functions result in 3-e, 4-e and 5-e integrals: e.g.

$$V_{xy}^{ij} = \langle xy|f_{12}Q_{12}r_{12}^{-1}|ij\rangle$$
$$= \langle xy|f_{12}(1 - O_1 - O_2 + O_1O_2 - V_1V_2)r_{12}^{-1}|ij\rangle$$

$$\sum_k \langle xyk|f_{12}r_{23}^{-1}|kji\rangle$$

O_1 and O_2 result in 3-e integrals

Introduce a large (but finite) complementary auxiliary basis CABS

$$Q_{12} \approx 1 - P_1P_2 - O_1V_2' - V_1'O_2$$

$$V_{xy}^{ij} \approx \langle xy|f_{12}(1 - P_1P_2 - V_1'O_2 + O_1V_2')r_{12}^{-1}|ij\rangle$$
$$\approx \langle xy|f_{12}r_{12}^{-1}|ij\rangle - \sum_{pq}\langle xy|f_{12}|pq\rangle\langle pq|r_{12}^{-1}|ij\rangle$$
$$- \sum_{ka'}\langle xy|f_{12}|ka'\rangle\langle ka'|r_{12}^{-1}|ij\rangle$$
$$- \sum_{a'k}\langle xy|f_{12}|a'k\rangle\langle a'k|r_{12}^{-1}|ij\rangle$$

	j	b	b'
i	HF	S	S'
a	S	D	D'
a'	S'	D'	D'

Many-electron integrals: V and X

	j	b	b'
i	HF	S	S'
a	S	D	D'
a'	S'	D'	D'

$$V_{xy}^{ij} = \langle \widetilde{xy} | f_{12} \hat{Q}_{12} r_{12}^{-1} | ij \rangle$$

$$X_{xy}^{vw} = \langle \widetilde{xy} | f_{12} \hat{Q}_{12} \hat{f}_{12} | \widetilde{vw} \rangle$$

$$\hat{Q}_{12} \approx Q_{12}^{A} = 1 - \sum_{pq} |pq\rangle\langle pq| - \sum_{ob'} |ob'\rangle\langle ob'| - \sum_{a'o} |a'o\rangle\langle a'o|$$

$$V_{xy}^{ij} = (fg)_{xy}^{ij} - r_{xy}^{pq} g_{pq}^{ij} - r_{xy}^{a'o} g_{a'o}^{ij} - r_{xy}^{ob'} g_{ob'}^{ij}$$

$$X_{xy}^{ij} = (f^2)_{xy}^{ij} - r_{xy}^{pq} r_{pq}^{ij} - r_{xy}^{a'o} r_{a'o}^{ij} - r_{xy}^{ob'} r_{ob'}^{ij}$$

For atoms, the RI truncates at $3L_{\mathrm{occ}}$ $\qquad r_{xy}^{ob'} = \mathcal{S}_{xy} \langle xy | f(r_{12}) | ob' \rangle$

scaling of contractions

opt	O^4V^2	O^5X
fix	O^2V^2	O^3X

Many-electron integrals: C

	j	b	b'
i	HF	S	S'
a	S	D	D'
a'	S'	D'	D'

$$C_{ab}^{vw} = \langle ab|(\hat{F}_1^0 + \hat{F}_2^0)\hat{Q}_{12}\hat{f}_{12}|\widetilde{vw}\rangle$$

$$\hat{Q}_{12} \approx \hat{Q}_{12}^B = \sum_{a'b'} |a'b'\rangle\langle a'b'| + \sum_{ab'} |ab'\rangle\langle ob'| + \sum_{a'b} |a'b\rangle\langle a'b|$$

$$C_{ab}^{vw} = f_a^{a'} r_{a'b}^{vw} + f_b^{b'} r_{ab'}^{vw}$$

For atoms, the RI truncates at L_{vir}

Need Fock matrix elements in CABS

Many-electron integrals: B

The B intermediate is more complicated - simple RI insertions converge slowly with the size of CABS

Apply commutator trick to $\langle \widetilde{xy}|f_{12}\hat{Q}_{12}\hat{F}^0_{12}\hat{Q}_{12}f_{12}|\widetilde{vw}\rangle$

$$\frac{1}{2}\langle \widetilde{xy}|f_{12}\hat{Q}_{12}[\hat{F}^0_{12}\hat{Q}_{12}]f_{12}|\widetilde{vw}\rangle + \frac{1}{2}\langle \widetilde{xy}|f_{12}[\hat{Q}_{12}\hat{F}^0_{12}]\hat{Q}_{12}f_{12}|\widetilde{vw}\rangle$$
$$\frac{1}{2}\langle \widetilde{xy}|f_{12}\hat{Q}_{12}[\hat{F}^0_{12}f_{12}]|\widetilde{vw}\rangle + \frac{1}{2}\langle \widetilde{xy}|[f_{12}\hat{F}^0_{12}]\hat{Q}_{12}f_{12}|\widetilde{vw}\rangle$$
$$\frac{1}{2}\langle \widetilde{xy}|f_{12}\hat{Q}_{12}f_{12}\hat{F}^0_{12}|\widetilde{vw}\rangle + \frac{1}{2}\langle \widetilde{xy}|\hat{F}^0_{12}f_{12}\hat{Q}_{12}f_{12}|\widetilde{vw}\rangle$$

First and last terms are simple

$$\langle \widetilde{xy}|f_{12}\hat{Q}_{12}[\hat{F}^0_{12}\hat{Q}_{12}]f_{12}|\widetilde{vw}\rangle = r^{ab}_{xy}C^{vw}_{ab}$$
$$\langle \widetilde{xy}|f_{12}\hat{Q}_{12}f_{12}\hat{F}^0_{12}|\widetilde{vw}\rangle = X^{vw}_{xy}(\varepsilon_v + \varepsilon_w)$$

Middle term requires care to avoid slowly convergent RI

$$\hat{Q}_{12}[\hat{F}^0_{12}, f_{12}] \approx \hat{Q}^A_{12}[\hat{T}_{12}, f_{12}] - \hat{Q}^B_{12}(\hat{K}_{12} + \hat{F}^1_{12})f_{12} + \hat{Q}^A_{12}f_{12}(\hat{K}_{12} + \hat{F}^1_{12})$$

Many-electron integrals: B

Middle term requires care to avoid slowly convergent RI

$$\tfrac{1}{2}\langle\widetilde{xy}|f_{12}\hat{Q}_{12}[\hat{F}^0_{12}f_{12}]|\widetilde{vw}\rangle + \tfrac{1}{2}\langle\widetilde{xy}|[f_{12}\hat{F}^0_{12}]\hat{Q}_{12}f_{12}|\widetilde{vw}\rangle$$

$$\hat{Q}_{12}[\hat{F}^0_{12}, f_{12}] \approx \hat{Q}^A_{12}[\hat{T}_{12}, f_{12}] - \hat{Q}^B_{12}(\hat{K}_{12} + \hat{F}^1_{12})f_{12} + \hat{Q}^A_{12}f_{12}(\hat{K}_{12} + \hat{F}^1_{12})$$

Contribution from $[\hat{T}_{12}, f_{12}] \gg [\hat{K}_{12}, f_{12}]$

$$[\hat{v}_n, f_{12}] = 0$$
$$[\hat{J}_{12}, f_{12}] = 0$$

Key to the success of the approximation is that the 2-electron integral for kinetic energy commutator is analytic

$$\tfrac{1}{2}[f_{12}, [\hat{T}_{12}, f_{12}]] = (\nabla_1 f_{12})^2$$

Cannot use $f_{12}\hat{Q}^A_{12}\hat{K}_{12}f_{12}$ since cannot evaluate $f_{12}\hat{K}_{12}f_{12}$

Should not use $f_{12}\hat{Q}^B_{12}f_{12}\hat{K}_{12}$ since RI is slowly convergent

The RI approximation: Summary

The RI approximation *truncates* or *converges rapidly* for some integrals, but cannot be used for others

$$\langle \phi_k \phi_{p''} | f_{12} | \phi_i \phi_j \rangle$$

only non-zero for an atom if $p'' \leq 3L_{\mathrm{occ}}$

$$\langle \phi_{p''} \phi_{q''} | f_{12} | \phi_i \phi_j \rangle$$

never truncates and is slowly converging

Through careful use of an ingenious commutator trick, Kutzelnigg, Klopper and Noga arrived at a stable formulation. A few new 2-electron integrals are required, but no 3-, 4- 5-electron integrals.

$$f_{12}, \qquad \frac{f_{12}}{r_{12}}, \qquad f_{12}^2, \qquad (\nabla_1 f_{12})^2$$

For $f_{12} = e^{-\gamma r_{12}}$ the integrals are analytic, but complicated. It is equally as efficient and accurate to expand using Gaussians

$$f_{12} = \sum_{\mu=1}^{6} c_\mu e^{-\gamma_\mu r_{12}^2} \approx e^{-\gamma r_{12}}$$

CABS singles correction to HF energies

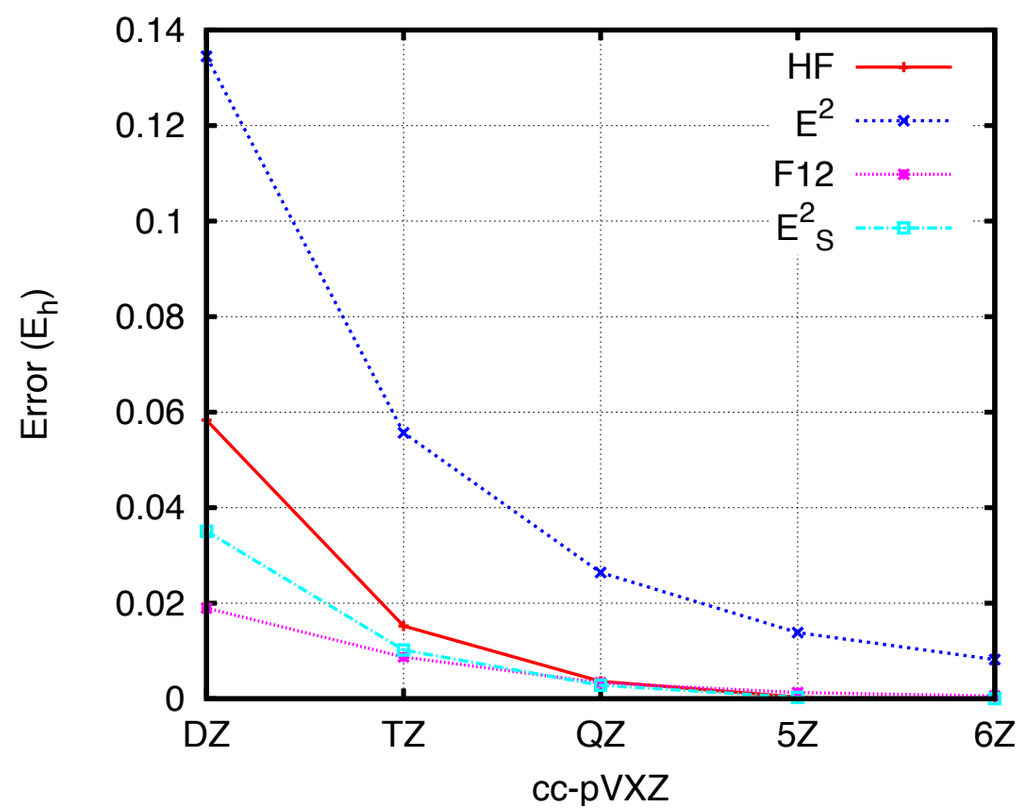
The basis set incompleteness error for E^2 is smaller than that of the underlying HF energy when computed with MP2-F12

Compute a 2nd order basis set incompleteness correction for HF

$$\begin{pmatrix} \delta_a^b(\epsilon_a - \epsilon_i) & f_a^{b'} \\ f_{a'}^b & f_{a'}^{b'} - \delta_{a'}^{b'}\epsilon_i \end{pmatrix} \begin{pmatrix} t_b^i \\ t_{b'}^i \end{pmatrix} = - \begin{pmatrix} f_a^i \\ f_{a'}^i \end{pmatrix}$$

$$E_S^2 = f_i^b t_b^i + f_i^{b'} t_{b'}^i$$

Fock matrix elements in the CABS basis are anyway computed



Cost of MP2-F12

Standard MP2: need cc-pVQZ basis

HF scales as $O(N^3)$ with a large prefactor

MP2 scales as $O(N^5)$ with a very small prefactor

MP2-F12: need cc-pVDZ basis (~4 times smaller)

Cost of HF reduced because smaller basis required

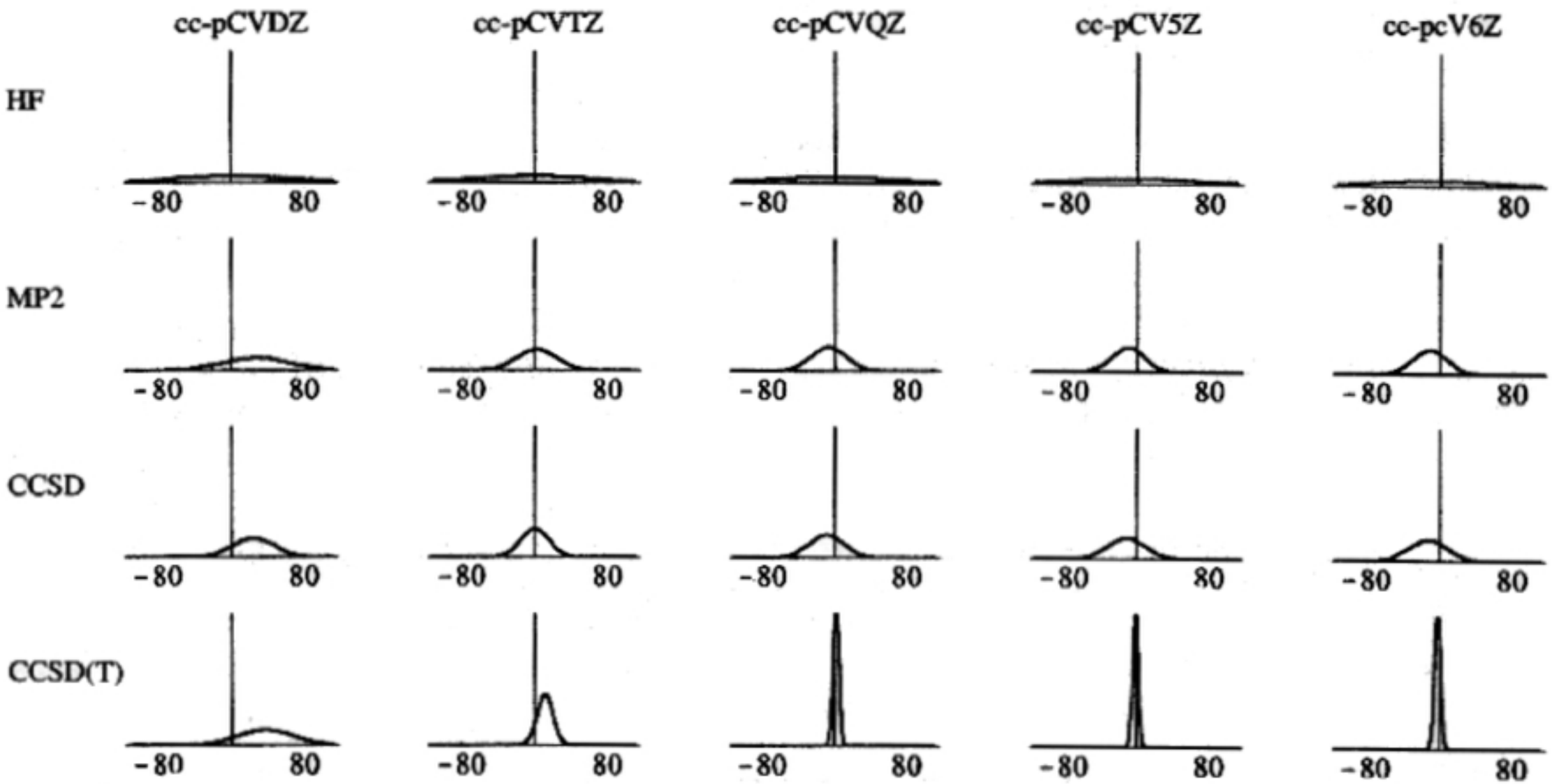
MP2-F12 scales as $O(N^5)$ with a very large prefactor

(>30 times MP2)

Since MP2 itself is only moderately accurate, it is rarely worthwhile doing MP2-F12 alone. It is usually combined with information from higher-order correlation treatments.

Comparison of basis set error and model error

Error statistics (kJ/mol) w.r.t experiment for 14 reaction energies of small molecules involving main group elements (c.f. Helgaker)



Large basis CCSD(T) calculations return accuracy of ~5 kJ/mol

F12 in higher-order methods: coupled-cluster

F12 Coupled Cluster wavefunction Ansatz

$$|\text{CCSD-F12}\rangle = e^T|0\rangle \qquad T = T_1 + T_2 + T_{2'}$$

$$E = \langle 0|He^T|0\rangle + \tfrac{1}{4}R_{ij}^{\alpha\beta}\langle {}^{\alpha\beta}_{ij}|e^{-T}He^T|0\rangle$$

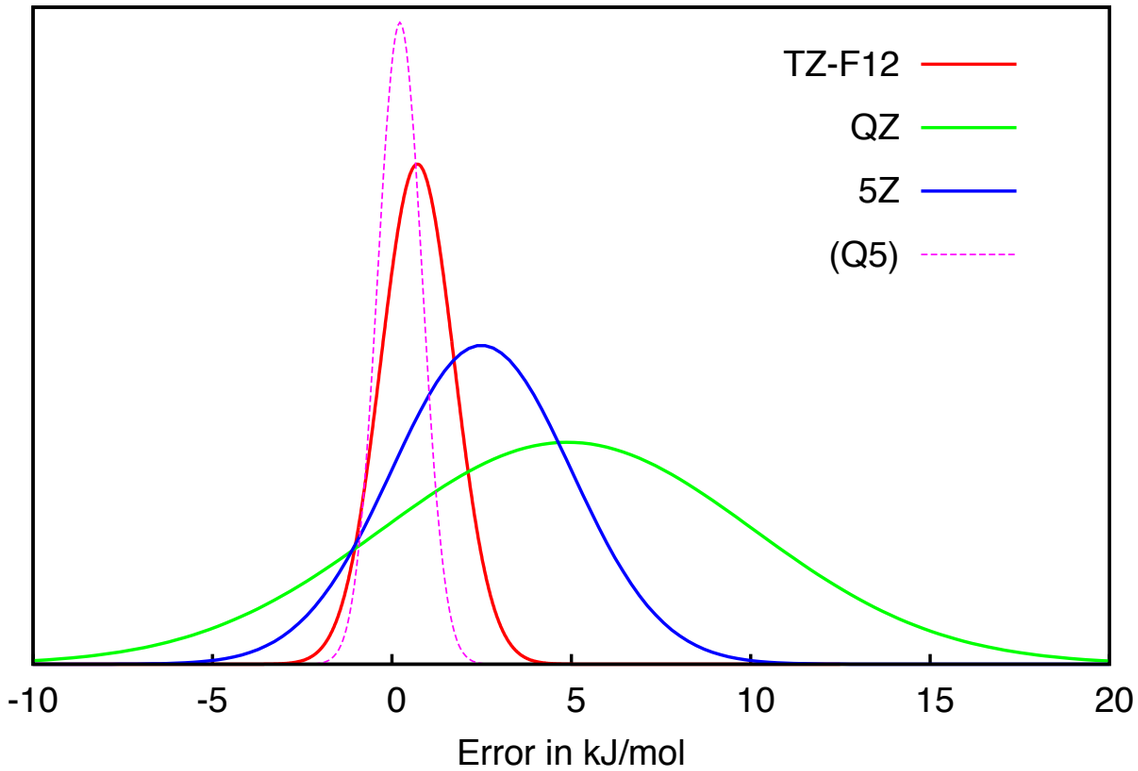
$$0 = \langle {}^{a}_{i}|e^{-T}He^T|0\rangle$$

$$0 = \langle {}^{ab}_{ij}|e^{-T}He^T|0\rangle$$

$$T_1 = \sum_{ia} T_i^a a_a^\dagger a_i$$

$$T_2 = \frac{1}{4}\sum_{ijab} T_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

$$T_{2'} = \frac{1}{4}\sum_{ij\alpha\beta} R_{ij}^{\alpha\beta} a_\alpha^\dagger a_\beta^\dagger a_j a_i$$



F12 overhead cost only ~15%

Comparison to post-FCI contributions

An illustrative example

The electron affinity of oxygen 1.4611 eV

ΔT = CCSDT – CCSD (5Z)
ΔQ = CCSDTQ – CCSDT (TZ)
ΔP = CCSDTQP – CCSDTQ (DZ)
ΔCCSD = CCSD-F12 – CCSD (5Z)

CCSD	T	Q	P	EA	ΔCCSD	EA
1.2654	0.1727	0.0121	-0.0008	1.4495	0.0197	1.4692

- Mass-Velocity-Darwin (MVD) – 0.0024
- Spin-orbit coupling – 0.0059
- Electron-nucleus dynamic coupling (non-adiabatic effects) + 0.0001

= 1.4610 eV

CCSD basis set incompleteness is larger than post CCSD(T) terms

Available F12 Methods

F12 can be combined with any electronic structure method that involves dynamic pair correlation. Basis set errors are reduced, equivalent to increasing the basis set by 2 Cardinal numbers.

- MP2-F12
- RPA-F12
- CCSD(T)-F12

Single reference

- CC2-F12
- EOM-CCSD-F12

Response properties

- CASPT2-F12
- MRCI-F12
- FCIQMC-F12

Multi-reference

F12 is now a standard method in quantum chemistry
TURBOMOLE, MOLPRO, DALTON, ORCA, GELLAN