Explicitly correlated wave functions

Wim Klopper and David P. Tew

Lehrstuhl für Theoretische Chemie
Institut für Physikalische Chemie
Universität Karlsruhe (TH)

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Outline

- Why we need explicitly correlated wave functions
- Hylleraas-type methods
- Exponentially correlated Gaussians
- The transcorrelated method
- Gaussian geminals
- The R12 method
- Quantum Monte Carlo

Accuracy *vs* Effort

- To rival experimental accuracy it is essential to reproduce the correlation between the motion of the electrons.
  - The mean-field HF method recovers 99% of the total energy, but the remaining 1% is critical for chemistry, especially if the bonding situation changes significantly.
- Correlation is included in coupled cluster wave functions by taking linear combinations of excited HF determinants.
  - The accuracy of the wave function is improved by increasing the number of determinants in the expansion.
  - Double excitations are most important, then singles and triples with minor contributions from higher excitations.
- For a given correlation method, the number of determinants depends on the number of HF orbitals, which is equal to the number of functions in the atomic orbital basis. How does the energy depend on the size of the orbital basis?

Orbital CI for He

- In a complete AO basis the CISD (or CCSD) method gives the exact energy for He.
- Principal quantum number.

n_{max}	Error (mE_h)
1	42.044
2	6.050
3	1.883
4	0.815
5	0.424
6	0.248
7	0.157
8	0.106

- Partial wave expansion.

l_{max}	Error (mE_h)
0	24.696
1	3.108
2	0.958
3	0.403
4	0.206
5	0.119
6	0.074
7	0.050

- The convergence with the AO basis is extremely slow. Chemical accuracy requires a cc-pV5Z basis or larger.
- The high angular momentum terms do not vanish since they are required to reproduce the electronic cusp.

Orbitals and the cusp condition

- The cusp condition dictates that as the coordinates of two electrons converge the wave function is linear in r_{12}.

$$\psi = (1 + \tfrac{1}{2} r_{12}) \psi_{r_{12}=0} + O(r_{12}^2) \qquad \text{(different spin electrons)}$$

- Orbital expansions introduce even powers of r_{12} into ψ.
- Consider the (spatial) 4 determinant expansion of He

$$\begin{aligned} \Phi &= 1s1s + c \sum_i 2p_i 2p_i \\ &= \exp(-\zeta_1(r_1 + r_2)) + c \exp(-\zeta_2(r_1 + r_2))(x_1x_2 + y_1y_2 + z_1z_2) \\ & \quad x_1x_2 + y_1y_2 + z_1z_2 = \mathbf{r}_1 \cdot \mathbf{r}_2 = \tfrac{1}{2}(r_1^2 + r_2^2 - r_{12}^2) \end{aligned}$$

- This is equivalent to the partial wave expansion of r_{12}, which requires high angular momentum for convergence.

$$r_{12} = \sum_{l=0}^{\infty} P_l(\cos\theta_{12}) \left(\frac{1}{2l+3} \frac{r_<^{l+2}}{r_>^{l+1}} - \frac{1}{2l+1} \frac{r_<^{l}}{r_>^{l-1}} \right)$$

The inter-electronic distance r_{12}

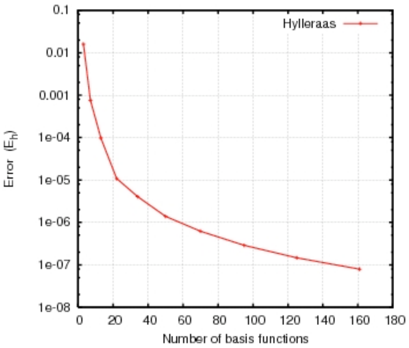
- Electron correlation is manifest through the dependence of the wave function on r_{12}, the inter-electronic distance.
- A more efficient description of electron correlation may be achieved if we include r_{12} explicitly in our expansion of ψ. For a given accuracy ψ will then require fewer parameters.
- In particular the cusp condition may be satisfied explicitly rather than through orbitals of high angular momenta.

- Methods that include r_{12} explicitly in the form of ψ are called *explicitly correlated methods*.

Hylleraas' method for He (1929)

- Hylleraas computed the energy of He to within 0.5 mE$_h$.
- His explicitly correlated wave function contained only six variational parameters.

$$\psi(r_1, r_2, r_{12}) = \exp(-\zeta s)(c_0 + c_1 r_{12} + c_2 r_{12}^2 + c_3 s + c_4 s^2 + c_5 t^2)$$



- In a Hylleraas CI expansion the basis functions are

$$s^i t^{2j} r_{12}^k e^{-\zeta s}$$

$$s = r_1 + r_2 \quad t = r_1 - r_2$$

and a basis is defined by n such that $i + 2j + k \leq n$.

- The convergence to the basis set limit is much faster than for orbital CI. Including all powers of r_{12} in the wave function form reduces the effort required for chemical accuracy from 120 to 13 CI terms.

Beyond Helium

- It is possible to extend the Hylleraas approach to 3-electron atoms in terms of the spatial basis functions

$$\Phi = r_1^i r_2^j r_3^k r_{12}^l r_{13}^m r_{23}^n \exp(-\alpha r_1 - \beta r_2 - \gamma r_3)$$

- Wave functions of this form have similar accuracy to those for helium.
- Computations of this type on molecules are much more complicated, the integrals are harder to solve.
- The James-Coolidge functions yield accurate solutions to the hydrogen molecule, in elliptic coordinates ξ_i, η_i, φ_i.

$$\Phi = \xi_1^k \eta_1^l \xi_2^m \eta_2^n r_{12}^m \exp(-\alpha(\xi_1 + \xi_2))$$

- These highly accurate wave functions are difficult to generalize to larger systems and the resulting integrals quickly become intractable.

Integrals involving r_{12}

- For n-electron wave functions we must evaluate n-electron integrals.
- The great simplification of orbital product based wave functions is that only 2-electron integrals are required.
- If we use functions that depend explicitly on r_{12} then we must be able to evaluate the resulting n-electron integrals.
- Due to the antisymmetry requirement the number of permutations of the n-electron integrals to evaluate grows as $n!$.
- There are various strategies for introducing explicit r_{12} dependence in a manageable way:
    - Gaussian r_{12} dependence with analytic integrals.
    - Using the transcorrelated Hamiltonian.
    - Computing the many-electron integrals approximately.
    - Using stochastic integration techniques.

Exponentially correlated Gaussians

- Consider the product of n 1-electron s-type Gaussians with exponents a_i at centers $\mathbf{C}_i$

$$\Phi(\mathbf{r}) = s_1(\mathbf{r}_1) \cdots s_n(\mathbf{r}_n) = \exp\left(-\sum_{i=1}^{n} a_i |\mathbf{r}_i - \mathbf{C}_i|^2\right)$$

- In *exponentially correlated Gaussians* explicit dependence on r_{12} is introduced into the n-electron basis function.

$$\Phi(\mathbf{r}) = \exp\left(-\sum_{i=1}^{n} a_i |\mathbf{r}_i - \mathbf{C}_i|^2 - \sum_{i<j=1}^{n} b_{ij} |\mathbf{r}_i - \mathbf{r}_j|^2\right) \qquad \text{(Boys)}$$

- The extra term correlates the motion of all pairs of electrons simultaneously. n-electron integration of these ECGs is straightforward due to the Gaussian form.

- The above ECG basis function may also be written as

$$\Phi(\mathbf{r}) = \exp\left(-\sum_{i,j=1}^{n} A_{ij}(\mathbf{r}_i - \mathbf{s}_i)\cdot(\mathbf{r}_j - \mathbf{s}_j)\right) \qquad \text{(Singer)}$$

- Defining an ECG $\Phi_k(\mathbf{r})$, with exponents A^k_{ij} and centers $\mathbf{s}^k_i$, in the ECG approach the wave function is expanded as

$$\begin{aligned}\Psi(\mathbf{r},\boldsymbol{\sigma}) &= \sum_k c_k \psi_k(\mathbf{r},\boldsymbol{\sigma}) \\ \psi_k(\mathbf{r},\boldsymbol{\sigma}) &= \hat{A}_n\left(\Phi_k(\mathbf{r})\Theta^n_{S,M_S}(\boldsymbol{\sigma})\right)\end{aligned}$$

- Ψ is variationally minimized with respect to all linear, c_k and nonlinear, $A^k_{ij}, s^k_{ix}, s^k_{iy}, s^k_{iz}$ parameters.
- The centers of the s-type Gaussians are permitted to float. $p, d\cdots$ functions are not required (for $\sum$ electronic states).

Excited states using ECGs

- The s-type ECGs are well suited for describing S electronic states of atoms and $\sum$ states of molecules.
- Excited states with S or $\sum$ symmetry correspond to the higher roots of the eigenvalue equations for c_k.
- For states with higher angular momenta it is sufficient to fix the centers at the node and augment the ECGs with a Cartesian prefactor.
- For atomic $\prod$ states one would use functions of the type

$$\Phi_k(\mathbf{r}) = y_1 \exp\left(-\sum_{i,j=1}^{n} A^k_{ij}\mathbf{r}_i\cdot\mathbf{r}_j\right)$$

- States of higher angular momentum are computed analogously.

Optimization of nonlinear parameters

- In the absence of symmetry each ECG basis function contains $n(n+7)/2$ nonlinear parameters.
  - $n(n+1)/2$ exponents A_{ij} and $3n$ centers s_{ix}, s_{iy}, s_{iz}.
- The variational minimization of the energy requires the optimization of a large number of nonlinear parameters.
- One possible strategy is to optimize smaller subspaces of parameters iteratively:
  - Chose an initial set of A_{ij}^k and s_i^k. (Random tempering)
  - Optimize c_k using linear algebra. (Davidson,Lanczos)
  - Optimize A_{ij}^k and s_i^k for one ECG basis function (Powell) with the rest fixed. Involves repeated integral evaluation and a knowledge of the derivatives.
  - Cycle over all basis functions.
  - Repeat until energy change is below a desired threshold.
- Both time consuming and tricky to get right.

Illustrative calculations: Li

Term	Energy (E_h)	Method
2^2S		
	-7.478060314	1536-term ECG
	-7.478060322	1589-term Hylleraas
2^2P		
	-7.4105622	3700-term ECG
	-7.4105651	1589-term Hylleraas

- This high accuracy makes it possible to study the tiny energy contributions from the nuclear charge distribution, or residual QED effects.
- Note that for the 2^2S ground state the 1536-term ECG contains 9216 nonlinear parameters, whereas the Hylleraas function contains only 3.

Illustrative calculations: H_2

- Rapid convergence for the GS of equilibrium H_2.

ECG basis	Energy (E_h)	ΔE (nE_h)
75	-1.17447472649	
150	-1.17447586067	1204.90
300	-1.17447592512	70.72
600	-1.17447593084	6.27
1200	-1.17447593121	0.55
2400	-1.17447593139	0.18
KW-883	-1.17447593074	

KW is a generalized James-Coolidge function.

- Analogous calculations for other bond distances and excited states enable the detailed study of the BO PES. E.g. double minima due to avoided crossings and the depths and positions of the vdW minima.

Summarizing the ECG method

Motivation: Integrals involving ECGs are (almost) all analytic.

Strategy: Variational minimization of linear and nonlinear parameters. The highly flexible s-type Gaussians adapt and shift to where they are most required.

Successes: Unrivaled accuracy for ground and excited state PES of small molecules (H_2, H_3, He_2^{+n}, LiH). Typically accurate to 9 significant figures with only a few thousand terms.

Limitations: The large number of nonlinear parameters and integral evaluations have prevented accurate calculations on systems with more than 4 electrons.

The transcorrelated method

- In this method we write $\psi(\mathbf{r},\boldsymbol{\sigma}) = J(\mathbf{r})\psi_0(\mathbf{r},\boldsymbol{\sigma})$

$$\begin{aligned} \psi_0(\mathbf{r},\boldsymbol{\sigma}) &= \hat{\mathcal{A}}_n\Big(\phi_1(\mathbf{r}_1,\sigma_1)\cdots\phi_n(\mathbf{r}_n,\sigma_n)\Big) \qquad \text{(single determinant)} \\ J(\mathbf{r}) &= \prod_{i<j}\text{exp}\Big(\sum_\kappa D_\kappa G_\kappa(\mathbf{r}_i,\mathbf{r}_j) + \sum_\lambda d_\lambda\left[g_\lambda(\mathbf{r}_i)+g_\lambda(\mathbf{r}_j)\right]\Big) \\ &= \text{exp}\Big(\sum_\kappa D_\kappa G_\kappa(\mathbf{r}) + 2\sum_\lambda d_\lambda g_\lambda(\mathbf{r})\Big) \quad = \text{exp}(C) \end{aligned}$$

- The idea is that J correlates the motion of the n-electrons and that ψ_0 should be close to the HF determinant.
- The 1- and 2-electron functions $g_\lambda(\mathbf{r}_i)$ and $G_\kappa(\mathbf{r}_i,\mathbf{r}_j)$ can be chosen to take any form.
- In the *transcorrelated method* all the nonlinear parameters D_κ and d_λ, and the orbitals ϕ_I are optimized.

Avoiding the n-electron integrals

- If we try to variationally minimize the Rayleigh quotient then $\langle\psi_0 J|\hat{H}|J\psi_0\rangle$ leads to n-electron integrals.
- Instead, the SE $\hat{H}J\psi_0 = EJ\psi_0$ is projected onto $\langle\psi_0 J^{-1}|$

$$\langle\psi_0|J^{-1}\hat{H}J|\psi_0\rangle = E$$

- $\hat{H}^C = J^{-1}\hat{H}J$ is called the *transcorrelated Hamiltonian*.
- Since $J = \text{exp}(C)$ we may BCH expand $\text{exp}(-C)\hat{H}\,\text{exp}(C)$

$\hat{H}$	$+\ [\hat{H},C]$	$+\ [[\hat{H},C],C]$	$+[[[\hat{H},C],C],C]$
$\frac{1}{2}\nabla_i^2$	$\frac{1}{2}\sum_{j\neq i}(\nabla_i^2 C_{ij} + 2\nabla_i C_{ij}\cdot\nabla_i)$	$\frac{1}{2}\sum_{jk\neq i}\nabla_i C_{ij}\cdot\nabla_i C_{ik}$	0
$-\frac{Z_I}{r_{iI}} + \frac{1}{r_{ij}}$	0	0	0

- $\hat{H}^C$ consists of only 1-, 2- and 3-electron operators so at most 3-electron integrals are required.
- Note that we can choose J so that $\hat{H}^C$ is cusp free.

- $\hat{H}^C$ is non Hermitian. Variationally optimizing the parameters can lead to energies below the exact value.
- The orbital parameters $X_{i\alpha}$ in $\phi_i = \sum_\alpha X_{i\alpha}\chi_\alpha$ and correlation parameters D_κ, d_λ are determined by solving

$$\begin{array}{rcll} \langle \frac{\partial\psi_0}{\partial X_{i\alpha}}|J^{-1}\hat{H}J - E|\psi_0\rangle & = & 0 & \text{singles} \\ \langle G_\kappa(\mathbf{r})\psi_0|J^{-1}\hat{H}J - E|\psi_0\rangle & = & 0 & \textit{doubles} \\ \langle g_\lambda(\mathbf{r})\psi_0|J^{-1}\hat{H}J - J\hat{H}J^{-1}|\psi_0\rangle & = & 0 & \text{singles} \end{array}$$

- The orbital equations are equivalent to SCF using $\hat{H}^C$.
- The functions G_κ involve single and double replacements

$$|G_\kappa(\mathbf{r})\psi_0\rangle = \sum_{AIBJ} G_{IJ}^{AB}|{}_{IJ}^{AB}\rangle + \sum_{AI} G_I^A|{}_I^A\rangle + G_0\psi_0$$

- Thus the correlation functions G_κ interfere with the orbitals.
- This redundancy is alleviated by the parameters d_λ, which satisfy the *contraction equations*. This makes $\hat{H}^C$ as Hermitian as possible in the space of single excitations.

Simplifications and extensions

- The above coupled equations can be largely decoupled by using the HF orbitals without reoptimization.
- The parameters d_λ are then related to the functions G_κ in a fixed way and the contraction equations are solved only once.
- The transcorrelated method then only involves the nonlinear optimization of a few parameters G_κ.

- The transcorrelated method need not be restricted to a single determinant.
- As a feasible alternative one could fix J such that the cusp condition is satisfied, and then use the cusp free transcorrelated Hamiltonian to optimize

$$\psi = J|\text{CC}\rangle \qquad \text{or} \qquad \psi = J|\text{CAS}\rangle$$

Illustrative calculations: Ne (1969)

- Choose functions for G_κ and g_λ such that the cusps are satisfied and the HF orbitals are decoupled at large r_{12}

$$\begin{aligned} G_1(\mathbf{r}_1,\mathbf{r}_2) &= \tfrac{1}{2}\frac{ar_{12}}{a+r_{12}} \qquad g_\lambda(\mathbf{r}_1) = \frac{\mathbf{r}_1}{a+r_1} \\ G_\kappa(\mathbf{r}_1,\mathbf{r}_2) &= (\bar{r}_1\bar{r}_2)^i(\bar{r}_1^i+\bar{r}_2^j)(\bar{\mathbf{r}}_1\cdot\bar{\mathbf{r}}_2)^k \\ \bar{\mathbf{r}}_i &= \frac{\mathbf{r}}{a+r} \end{aligned}$$

- Use Slater functions for the orbital basis.
- Numerical integration of the 3-electron integrals.

	Experimental	predicted	error
Ne	-128.929	-128.959	-0.030
Ne^+	-128.138	-128.166	-0.028
IP	0.791	0.793	0.002

Illustrative calculations: LiH, H_2O (1972)

- Choose Gaussian functions for G_κ, g_λ and orbitals. 3-electron integrals are then analytic.

$$\begin{aligned} G_\kappa(\mathbf{r}_1,\mathbf{r}_2) &= \exp(-a_\kappa r_{12}^2 - b_\kappa r_{1B_\kappa}^2 - c_\kappa r_{1C_\kappa}^2) \\ g_\lambda(\mathbf{r}_1) &= \exp(-p_\lambda r_{1P_\lambda}^2) \\ \chi_\alpha(\mathbf{r}_1) &= \exp(-q_\alpha r_{1Q_\alpha}^2) \end{aligned}$$

- Choose the centers B_κ, C_κ, P_λ, Q_α to be located at one of the nuclei. Define a basis by selecting the exponents a_κ, b_κ, c_κ, p_λ, q_α.

	E_{corr}	Exact(1972)
LiH	-0.076	-0.082
H_2O	-0.254	-0.364

- Note that even though the HF orbitals used in these calculations are very poor approximations to the true HF orbitals, reasonable correlation energies result.

Gaussian geminals

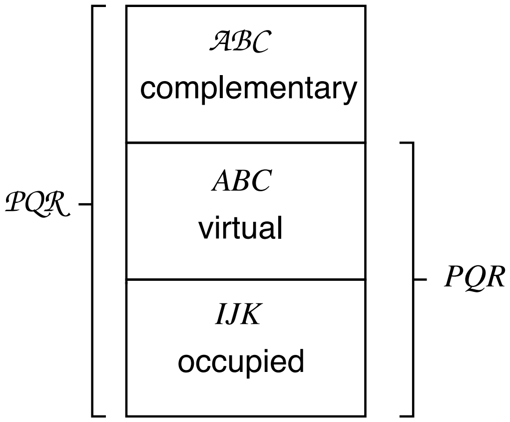
- The n-electron integration required for the ECG method is reduced to at most 4-electron integration if each n-electron basis function correlates only 2 electrons explicitly. E.g.

$$\begin{aligned}\Phi_k(\mathbf{r}) &= \exp\left(-\sum_{i=1}^{n} a_i^k|\mathbf{r}_i - \mathbf{C}_i^k|^2 - b^k|\mathbf{r}_1 - \mathbf{r}_2|^2\right) \\ &= \exp(-b^k r_{12}^2) s_1^k(\mathbf{r}_1) \cdots s_n^k(\mathbf{r}_n)\end{aligned}$$

- This also reduces the number of nonlinear parameters in a variational calculation.
- The computation of 4-electron integrals is nonetheless expensive and this method has received little attention.
- Gaussian geminals are mostly applied in the framework of pair theories such as MP2, CCD, etc.

The formally complete one-electron basis

- To use second quantization in the discussion of explicitly correlated wavefunctions in pair theories we introduce the concept of the *formally complete one electron basis*.
  - The infinite set of one-electron functions, which can be used to express the exact solutions to the Fock equation.



- This spin-orbital notation will be used throughout this lecture.

Gaussian geminals as pair clusters

- For a formally complete set of virtual orbitals

$$|\text{CCD}\rangle = \exp(\hat{T}_2)|\text{HF}\rangle \qquad \hat{T}_2 = \tfrac{1}{2}\sum_{\mathcal{A}I\mathcal{B}J} t_{IJ}^{\mathcal{A}\mathcal{B}}\hat{\tau}_{IJ}^{\mathcal{A}\mathcal{B}}$$

  - $\mathcal{A}\mathcal{B}$ label the infinite set of virtual orbitals.
- The convergence of finite virtual orbital sets to the exact limit is slow. We replace the set of virtual orbital pairs with a set of explicitly correlated Gaussian geminals.
- In first quantization

$$\left\{\phi_{\mathcal{A}}(\mathbf{x}_1)\phi_{\mathcal{B}}(\mathbf{x}_2)\right\} \rightarrow \left\{\hat{Q}_{12}\varphi_k(\mathbf{x}_1,\mathbf{x}_2)\right\}$$

$$\begin{aligned}
\varphi_k(\mathbf{x}_1,\mathbf{x}_2) &= \hat{\mathcal{A}}_2\left(\Phi_k(\mathbf{r}_1,\mathbf{r}_2)\Theta_k(\sigma_1,\sigma_2)\right)\\
\Phi_k(\mathbf{r}_1,\mathbf{r}_2) &= \exp(-br_{12}^2)\chi_1^k(\mathbf{r}_1)\chi_2^k(\mathbf{r}_2)\\
\chi_i^k(\mathbf{r}_i) &= x_{iC_i^k}^{l_k}y_{iC_i^k}^{m_k}z_{iC_i^k}^{n_k}\exp(-a_i^k|\mathbf{r}_i-\mathbf{C}_i^k|^2)
\end{aligned}$$

- Note that the orbitals $\mathcal{A}\mathcal{B}$ are orthogonal to IJ. The operator $\hat{Q}_{12}$ imposes this *strong orthogonality condition* on the Gaussian geminals.

$$\hat{Q}_{12} = (1-\hat{O}_1)(1-\hat{O}_2) \qquad \hat{O} = \sum_I |\phi_I\rangle\langle\phi_I|$$

- The 2nd quantization representation of a HF determinant with one orbital pair replaced by a Gaussian geminal is

$$\sum_{\mathcal{A}\mathcal{B}} \bar{G}_k^{\mathcal{A}\mathcal{B}}|{}_{IJ}^{\mathcal{A}\mathcal{B}}\rangle \equiv \sum_{\mathcal{A}\mathcal{B}} \bar{G}_k^{\mathcal{A}\mathcal{B}}\hat{\tau}_{IJ}^{\mathcal{A}\mathcal{B}}|HF\rangle \qquad \bar{G}_{\mathcal{A}\mathcal{B}}^k = \langle\phi_{\mathcal{A}}\phi_{\mathcal{B}}|\varphi_k\rangle$$

- The cluster operator now involves amplitudes c_k^{IJ} for the excitation of IJ into a Gaussian geminal k.

$$\hat{T}_2 = \tfrac{1}{4} \sum_{k\mathcal{A}I\mathcal{B}J} c_k^{IJ} \bar{G}_k^{\mathcal{A}\mathcal{B}} \hat{\tau}_{IJ}^{\mathcal{A}\mathcal{B}}$$

  - In general different sets of φ_k can be used for each IJ.
- The CCD energy becomes

$$\begin{aligned} E &= \langle \text{HF}|\hat{H}^{T_2}|\text{HF}\rangle \\ &= E_{HF} + \langle \text{HF}|\hat{\Phi}\hat{T}_2|\text{HF}\rangle \\ &= E_{HF} + \tfrac{1}{4} \sum_{k\mathcal{A}I\mathcal{B}J} c_k^{IJ} \bar{G}_k^{\mathcal{A}\mathcal{B}} \langle IJ|\hat{\Phi}|\mathcal{A}\mathcal{B}\rangle \\ &= E_{HF} + \tfrac{1}{4} \sum_{k\mathcal{A}I\mathcal{B}J} c_k^{IJ} \bar{G}_k^{\mathcal{A}\mathcal{B}} \bar{g}_{\mathcal{A}\mathcal{B}}^{IJ} \end{aligned}$$

- The equations for the amplitudes c_k^{IJ} are obtained by projecting the coupled cluster Schrödinger equation onto the doubles manifold spanned by the geminals.

$$\begin{aligned} 0 &= \langle \mu_2|\hat{H}^{T_2}|\text{HF}\rangle = \langle \mu_2|[\hat{H},\hat{T}_2]|\text{HF}\rangle + \tfrac{1}{2}\langle \mu_2|[[\hat{H},\hat{T}_2],\hat{T}_2]|\text{HF}\rangle \\ &= \sum_{\mathcal{A}\mathcal{B}} \bar{G}_k^{\mathcal{A}\mathcal{B}} \left[\langle {}^{\mathcal{A}\mathcal{B}}_{IJ}|[\hat{H},\hat{T}_2]|\text{HF}\rangle + \tfrac{1}{2}\langle {}^{\mathcal{A}\mathcal{B}}_{IJ}|[[\hat{H},\hat{T}_2],\hat{T}_2]|\text{HF}\rangle \right] \end{aligned}$$

- Only the first term is present in MP2 and LCCD. For simplicity we write the amplitude equations as

$$\begin{aligned} 0 &= \tfrac{1}{2} \sum_{\mathcal{A}\mathcal{B}l} \bar{G}_k^{\mathcal{A}\mathcal{B}} F_{\mathcal{A}\mathcal{B}}^{l} c_l^{IJ} + \tfrac{1}{2} \sum_{\mathcal{A}\mathcal{B}} \bar{G}_k^{\mathcal{A}\mathcal{B}} V_{\mathcal{A}\mathcal{B}}^{IJ} \\ F_{\mathcal{A}\mathcal{B}}^{l} &= \sum_{\mathcal{C}} [f_{\mathcal{A}}^{\mathcal{C}} \bar{G}_{\mathcal{C}\mathcal{B}}^{l} + f_{\mathcal{B}}^{\mathcal{C}} \bar{G}_{\mathcal{A}\mathcal{C}}^{l}] - (\varepsilon_I + \varepsilon_J) \bar{G}_{\mathcal{A}\mathcal{B}}^{l} \end{aligned}$$

- $V_{\mathcal{A}\mathcal{B}}^{IJ}$ (long) contains terms linear and quadratic in c_k^{IJ}.
- The amplitude equations are solved iteratively

$$0 = \sum_{\mathcal{A}\mathcal{B}l} \bar{G}_k^{\mathcal{A}\mathcal{B}} F_{\mathcal{A}\mathcal{B}}^{l} c_l^{IJ\,[n+1]} + \sum_{\mathcal{A}\mathcal{B}} \bar{G}_k^{\mathcal{A}\mathcal{B}} V_{\mathcal{A}\mathcal{B}}^{IJ}(\mathbf{c}^{[n]})$$

Gaussian geminals: many electron integrals

- The above equations contain 3-, 4- and 5-electron integrals
- From the resolution of the identity we have

$$\sum_{\mathcal{PQ}} |\mathcal{PQ}\rangle\langle\mathcal{PQ}| = 1 \qquad \mathcal{PQ}\text{ span the complete basis}$$

$$= \sum_{\mathcal{AB}} |\mathcal{AB}\rangle\langle\mathcal{AB}| + \sum_{I\mathcal{Q}} |I\mathcal{Q}\rangle\langle I\mathcal{Q}| + \sum_{\mathcal{P}J} |\mathcal{P}J\rangle\langle\mathcal{P}J| - \sum_{IJ} |IJ\rangle\langle IJ|$$

- Consider $\sum_{\mathcal{AB}} \bar{G}_k^{\mathcal{AB}} \bar{g}^{IJ}_{\mathcal{AB}} = \sum_{\mathcal{AB}} \langle\phi_I\phi_J|\hat{\Phi}|\phi_{\mathcal{A}}\phi_{\mathcal{B}}\rangle\langle\phi_{\mathcal{A}}\phi_{\mathcal{B}}|\varphi_k\rangle$

$$= \langle\phi_I\phi_J|\hat{\Phi}|\phi_k\rangle - \sum_{M\mathcal{Q}} \langle\phi_I\phi_J|\hat{\Phi}|\phi_M\phi_{\mathcal{Q}}\rangle\langle\phi_M\phi_{\mathcal{Q}}|\varphi_k\rangle$$

$$-\sum_{\mathcal{P}N} \langle\phi_I\phi_J|\hat{\Phi}|\phi_{\mathcal{P}}\phi_N\rangle\langle\phi_{\mathcal{P}}\phi_N|\varphi_k\rangle + \sum_{MN} \langle\phi_I\phi_J|\hat{\Phi}|\phi_M\phi_N\rangle\langle\phi_M\phi_N|\varphi_k\rangle$$

- The second and third terms are 3-electron integrals. They arise due to the strong orthogonality (SO) projector.

- In general, a contraction over one or more indices $\mathcal{AB}\cdots$ involving two operators such as $\bar{G}$ or f gives rise to 3-electron integrals.
- A further contraction over $\mathcal{AB}\cdots$ involving another operator results in 4-electron integrals, and so on.
- The CCD energy evaluation requires 3-electron integrals and the amplitude equations involve 3-, 4- and 5-electron integrals.

$$\sum_{\mathcal{ABC}} \bar{G}_k^{\mathcal{AB}} f_{\mathcal{A}}^{\mathcal{C}} \bar{G}^l_{\mathcal{CB}} \quad \rightarrow \quad \text{4-electron integrals}$$

$$\sum_{\mathcal{AB}} \bar{G}_k^{\mathcal{AB}} V^{IJ}_{\mathcal{AB}} \quad \rightarrow \quad \text{3-, 4- and 5-electron integrals}$$

- The 4- and 5-electron integrals prevent larger scale applications and approximations are made to avoid them.

Removing the 4- and 5-electron integrals

- The 5-electron integrals only arise in two terms that depend quadratically on the amplitudes. They are expected to be small and are simply neglected → FCCD.
- All of the 4-electron integrals in the MP2 and LCCD are removed by the *weak orthogonality* (WO) and *super weak orthogonality* (SWO) approximations respectively.
- In the WO approximation the SO projector is removed and replaced by a penalty function for nonorthogonality.

$$-\tfrac{1}{2}\bar{G}_k^{\mathcal{AB}}\left(f_{\mathcal{A}}^{\mathcal{C}}\bar{G}_{\mathcal{CB}}^{l} + f_{\mathcal{B}}^{\mathcal{C}}\bar{G}_{\mathcal{AC}}^{l} - (\varepsilon_I+\varepsilon_J)\bar{G}_{\mathcal{AB}}^{l}\right)c_l^{IJ} = \tfrac{1}{2}\bar{G}_k^{\mathcal{AB}}V_{\mathcal{AB}}^{IJ}$$

$$-\tfrac{1}{2}\bar{G}_k^{\mathcal{PQ}}\left(\tilde{f}_{\mathcal{P}}^{\mathcal{R}}\bar{G}_{\mathcal{RQ}}^{l} + \tilde{f}_{\mathcal{Q}}^{\mathcal{R}}\bar{G}_{\mathcal{PR}}^{l} - (\varepsilon_I+\varepsilon_J)\bar{G}_{\mathcal{PQ}}^{l}\right)c_l^{IJ} = \tfrac{1}{2}\bar{G}_k^{\mathcal{AB}}V_{\mathcal{AB}}^{IJ}$$

  - $\tilde{\hat{f}} = \hat{f} + \left(\tfrac{1}{2}(\varepsilon_I-\varepsilon_J) - \varepsilon_{\text{min}} + \eta\right)\hat{O}_1$

- The energy is still an upper bound and in the limit of a complete geminal basis the exact energy is still obtained.
- Large values of η are required to prevent the pair functions becoming contaminated with HF orbital pairs.
- The parameter η may be removed if one approximately projects out this contamination from the amplitudes in each iteration (WOP).
- The super weak orthogonality approximation involves the replacement

$$\tfrac{1}{2}\bar{G}_k^{\mathcal{AB}}V_{\mathcal{AB}}^{IJ} \quad\rightarrow\quad \tfrac{1}{2}\bar{G}_k^{\mathcal{PQ}}\tilde{V}_{\mathcal{PQ}}^{IJ} - \tfrac{1}{2}\bar{G}_k^{\mathcal{MN}}\tilde{V}_{\mathcal{MN}}^{IJ}$$

- where $\tilde{V}$ indicates that V has been derived without invoking the SO projector.
- The SWOP-FCCD approach is an approximate CCD method where only 3-electron integrals need be evaluated.
- Approximate CCSD approaches are also available.

Two methods using Gaussian geminals

- The HF wave function is optimized in an orbital basis.

1. *Optimize* the Gaussian geminal basis by varying the nonlinear parameters.
   - Choose an initial set of (random tempered) exponents and centers for the Gaussian geminals.
   - Evaluate the integrals and compute the MP2 or CCD etc amplitudes c_k^{IJ} by solving the amplitude equations iteratively.
   - Optimize the nonlinear parameters using fixed amplitudes.
   - Repeat cycle until converged to within a desired threshold.
2. Define a *fixed* Gaussian basis by choosing a set of exponents b in a Gaussian correlation factor multiplying HF orbitals.

$$\Phi_k(\mathbf{r}_1, \mathbf{r}_2) = \exp(-br_{12}^2)\phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_2)$$

   - Evaluate the integrals, solve the (MP2, CCD etc) amplitude equations iteratively and compute the energy.

Illustrative calculations

FCCD correlation energies.

	E_{corr} (mE_h)	Method
LiH		
	-82.843	GTG
	-82.834	R12
Ne		
	-378.66	GTG
	-381.03	R12

MP2 correlation energies.

	6 GTG	exact
CH_4	-210.16	-218.91
C_2H_2	-393.15	-404.68
C_2H_4	-358.77	-373.67
H_2CO	-423.75	-448.21
N_2H_4	-467.37	-498.32

- Optimizing nonlinear parameters
- High accuracy with few geminals.
- Restricted to very small systems.

- 6 GTGs, no nonlinear parameters.
- 90% accuracy using DZ HF basis.
- Restricted to small molecules.

Summarizing the Gaussian geminal method

Motivation: The $n!$ growth of the number of n-electron integrals is avoided by using Gaussian geminals in the context of cluster functions.

Strategy: The large basis of virtual pair functions is replaced by a much smaller set of geminal ECGs. Near basis set limit correlation energies for the selected cluster model are obtained by optimizing of the nonlinear parameters.

Successes: Basis set limit CCSD, MP2, MP3 etc correlation energies for very small molecules, typically with μE$_h$ accuracy.

Limitations: The cost of evaluating numerous 3- and 4-electron integrals restricts calculations to at most 10 electron systems.

The linear R12 method

- We make the observation that
  - The overall shape of ψ is well described in CC methods.
  - Only the cusp is not well reproduced, leading to slow convergence.
- In R12 methods explicitly correlated geminal functions that can describe the cusp are added to the orbital basis.
  - Contrast with the GTG method where the virtual orbitals are entirely replaced by Gaussian geminals.
- The cusp condition for electron coalescence means that

$$\psi(r_{12}\approx 0) \;=\; \psi(r_{12}=0) + c_s r_{12}\psi(r_{12}=0) + O(r_{12}^2)$$

- ψ_{HF} is usually a good zeroth order approximation to ψ and the functions $\hat{\mathcal{A}}_n(r_{12}\phi_1(\mathbf{x}_1)\cdots\phi_n(\mathbf{x}_n))$ are well suited for describing the cusp (all other particles well separated).

- In the language of first quantization this corresponds to increasing the basis of pair functions

$$\{\phi_P\phi_Q\} \quad \rightarrow \quad \{\phi_P\phi_Q\} + \{r_{12}\phi_I\phi_J\}$$

- r_{12} is a 2-electron operator that acts on $\phi_I\phi_J$. In second quantization the operator r_{12} is represented by

$$\frac{1}{2}\sum_{\mathcal{PQRS}} r_{\mathcal{PQRS}}a^\dagger_{\mathcal{P}}a^\dagger_{\mathcal{R}}a_{\mathcal{S}}a_{\mathcal{Q}} \qquad r_{\mathcal{PQRS}} = r^{\mathcal{PR}}_{\mathcal{QS}} = \langle\mathcal{PR}|r_{12}|\mathcal{QS}\rangle$$

  - $\mathcal{PQRS}$ span the formally complete basis.
- Acting r_{12} on $|IJ\rangle$ gives the pair function $r_{12}|IJ\rangle$

$$\frac{1}{2}\sum_{\mathcal{PQRS}} r^{\mathcal{PR}}_{\mathcal{QS}}a^\dagger_{\mathcal{P}}a^\dagger_{\mathcal{R}}a_{\mathcal{S}}a_{\mathcal{Q}}a^\dagger_I a^\dagger_J|\text{vac}\rangle = \frac{1}{2}\sum_{\mathcal{PR}}\bar{r}^{\mathcal{PR}}_{IJ}a^\dagger_{\mathcal{P}}a^\dagger_{\mathcal{R}}|\text{vac}\rangle$$

- There is a substantial overlap between the conventional orbital basis $\{\phi_P\phi_Q\}$ and the R12 geminals $\{r_{12}\phi_I\phi_J\}$ which could lead to linear dependencies.

- We redefine our R12 geminal pair functions, introducing a projector so that they are orthogonal to the orbital basis.

$$r_{12} \rightarrow \hat{Q}_{12}r_{12} \qquad \hat{Q}_{12} = \sum_{\mathcal{AB}}|\mathcal{AB}\rangle\langle\mathcal{AB}|$$

- In second quantization the pair function $\hat{Q}_{12}r_{12}|IJ\rangle$ is

$$\frac{1}{2}\sum_{\mathcal{AB}}\bar{r}^{\mathcal{AB}}_{IJ}a^\dagger_{\mathcal{A}}a^\dagger_{\mathcal{B}}|\text{vac}\rangle$$

- Now let us consider the pair clusters in CC theory

$$a^\dagger_I a^\dagger_J \rightarrow a^\dagger_I a^\dagger_J + \sum_{A>B} t^{AB}_{IJ}a^\dagger_A a^\dagger_B + \frac{1}{2}\sum_{K>L} c^{KL}_{IJ}\sum_{\mathcal{AB}}\bar{r}^{\mathcal{AB}}_{KL}a^\dagger_{\mathcal{A}}a^\dagger_{\mathcal{B}}$$

- There are additional amplitudes c^{KL}_{IJ} that represent the probability of the excitation of pair IJ into the combination of states represented by $\hat{Q}_{12}r_{12}|KL\rangle$

CC-R12 methods

- In R12 methods a R12 doubles excitation operator $\hat{T}_{2'}$ is added to the conventional cluster operator $\hat{T}$.

$$|\text{CC-R12}\rangle = \exp(\hat{T}_{R12})|\text{HF}\rangle \qquad \hat{T}_{R12} = \hat{T} + \hat{T}_{2'}$$

$$\hat{T}_{2'} = \tfrac{1}{4} \sum_{IJKL} c_{IJ}^{KL} \sum_{\mathcal{AB}} \bar{r}_{KL}^{\mathcal{AB}} a_{\mathcal{A}}^{\dagger} a_I a_{\mathcal{B}}^{\dagger} a_J = \tfrac{1}{4} \sum_{IJKL} c_{IJ}^{KL} \hat{\mathcal{R}}_{IJ}^{KL}$$

- The amplitudes c_{IJ}^{KL} are determined by projecting the Schrödinger equation onto the doubles manifold spanned by the R12 geminals

$$0 = \tfrac{1}{2} \sum_{\mathcal{AB}} \bar{r}_{IJ}^{\mathcal{AB}} \langle {}_{IJ}^{\mathcal{AB}} | \hat{H}^{T_{R12}} | \text{HF} \rangle$$

- The energy is $\quad E = \langle \text{HF} | \hat{H}^{T_{R12}} | \text{HF} \rangle$
- R12 is easily applied to all CC methods (plus response). The difficulty lies in computing the R12 contributions.

R12 geminals: many electron integrals

- In the same way as for Gaussian geminals the CC-R12 equations involve 3-, 4- and 5-electron integrals.
- As an example, let us consider the term

$$\tfrac{1}{2} \sum_{\mathcal{AB}} \bar{r}_{KL}^{\mathcal{AB}} \langle {}_{IJ}^{\mathcal{AB}} | [\hat{F}, \hat{T}_{2'}] | \text{HF} \rangle =$$

$$\tfrac{1}{2} \sum_{\mathcal{ABMN}} \bar{r}_{IJ}^{\mathcal{AB}} \Big(\sum_{\mathcal{C}} (f_{\mathcal{A}}^{\mathcal{C}} \bar{r}_{\mathcal{CB}}^{MN} + f_{\mathcal{B}}^{\mathcal{C}} \bar{r}_{\mathcal{AC}}^{MN}) - (\varepsilon_i + \varepsilon_j) \bar{r}_{\mathcal{AB}}^{MN} \Big) c_{MN}^{IJ}$$

$$= \sum_{\mathcal{MN}} \left(\bar{F}_{KL}^{\mathcal{MN}} - (\varepsilon_i + \varepsilon_j) \bar{X}_{KL}^{MN} \right) c_{MN}^{IJ}$$

- $\bar{X}_{KL}^{MN}$ is the overlap between two R12 geminals and requires 3-electron integration due to $\hat{Q}_{12}$.

$$\bar{X}_{KL}^{MN} = \tfrac{1}{2} \sum_{\mathcal{AB}} \bar{r}_{KL}^{\mathcal{AB}} \bar{r}_{\mathcal{AB}}^{MN} = \langle KL | r_{12} \hat{Q}_{12} r_{12} | MN \rangle$$

The approximate resolution of the identity

- In contrast to Gaussian geminals the many electron integrals cannot be evaluated analytically. Instead the *approximate resolution of the identity* is applied successively so that only two electron integrals remain.
- Consider again the overlap matrix $\bar{X}_{KL}^{MN}$

$$\begin{aligned} \bar{X}_{KL}^{MN} &= \langle KL|r_{12}r_{12}|MN\rangle + \sum_{PQ}\langle KL|r_{12}|PQ\rangle\langle PQ|r_{12}|MN\rangle \\ &\quad - \sum_{P}\langle KLP|r_{12}r_{23}|PNM\rangle - \sum_{Q}\langle KLQ|r_{12}r_{13}|MQN\rangle \end{aligned}$$

- We introduce a large finite auxiliary orbital basis $\{\phi_{P'}\}$ such that the resolution of the identity is approximately fulfilled in this basis.

$$1 \approx \sum_{P'} |P'\rangle\langle P'|$$

- Wherever we have two operators that are linked by only one coordinate we insert an approximate resolution of the identity

$$r_{12}r_{13} \approx \sum_{P'} r_{12}|P_1'\rangle\langle P_1'|r_{13}$$

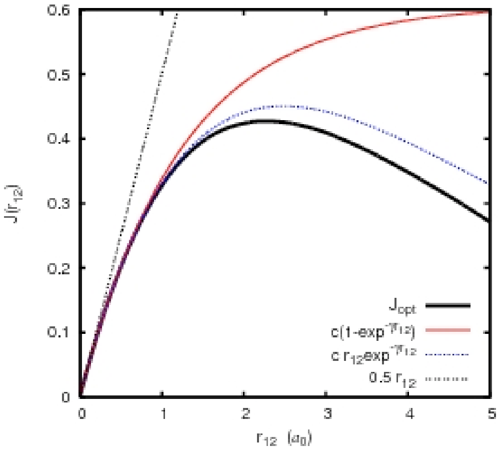
- The 3-electron integral becomes a sum of products of two 2-electron integrals

$$\langle KLQ|r_{12}r_{13}|MQN\rangle = \sum_{P'}\langle KL|r_{12}|P'Q\rangle\langle P'Q|r_{13}|MN\rangle$$

- In this way all 3-, 4- and 5-electron integrals may be approximately evaluated using only 2-electron integrals, which are available in conventional integral packages.
- Further approximations, such as the generalized Brillouin condition, are also used to simplify the R12 equations.

Beyond linear R12

- The way the many-electron integrals are evaluated in R12 theory can be applied to any geminal functions, provided that the required 2-electron integrals are available.
- Linear R12 geminal functions give a good description of ψ close to the cusp, but are inappropriate at larger r_{12}.
- It is much better to replace linear r_{12} with $\exp(-r_{12})$ (F12)



- The geminals $\exp(-r_{12})|IJ\rangle$ are able to describe the shape of ψ over a wider range of r_{12}.
- The 2-electron integrals involved are (almost) analytic, but complicated. It is easy to fit $\exp(-r_{12})$ using Gaussians.

Illustrative calculations

- MP2-R12 and MP2-F12 correlation energies using aug-cc-pVXZ basis sets.

Molecule	Basis	MP2-R12	MP2-F12
Thiophene	aVDZ		-0.887751
C_5SH_4	aVTZ		-0.909028
	aVQZ	-0.893074	-0.914260
	limit	-0.9164(16)	-0.9164(16)
Urea	aVDZ		-0.892774
CN_2OH_4	aVTZ		-0.911071
	aVQZ	-0.901119	-0.915838
	limit	-0.9178(13)	-0.9178(13)

- Currently CCSD(T)-R12 calculations an be performed using 1000 basis functions and correlating 20 electrons.

Variational Monte Carlo

- In VMC the n-dimensional integration of a fully correlated ψ is performed using Monte Carlo (stochastic) integration.
- A trial ψ is selected, e.g. $J\psi_0$, and the nonlinear parameters are varied to minimize the energy.
- MC integration is appropriate for evaluating expectation values of multiplicative operators $\hat{A}(\mathbf{x})$.
- The expectation value $\langle A \rangle$ is the weighted average of $A(\mathbf{x})$ over all space.

$$\langle A \rangle = \int A(\mathbf{x})\psi^2(\mathbf{x})d\mathbf{x}$$

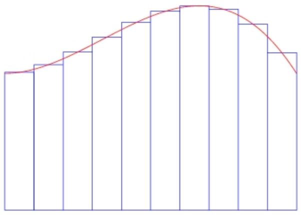
- Each point $\mathbf{x}$ has a weight $\psi^2(\mathbf{x})$, the probability of the particles being found at $\mathbf{x}$.
- The energy is evaluated by averaging the local energy

$$E_L(\mathbf{x}) = \frac{\hat{H}\psi(\mathbf{x})}{\psi(\mathbf{x})}$$

Monte Carlo integration

- The familiar trapezium rule for numerical integration is

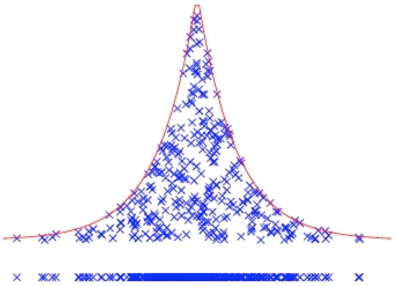
$$\int_0^1 A(x)dx \approx \frac{1}{N}\sum_{i=1}^{N} A(x_i)$$



- MC integration sums over N randomly generated (evenly distributed) points, instead of regularly spaced points.
- Both are exact in the limit $N \to \infty$
- To evaluate expectation values $\langle A \rangle$ that involve integration over all space we define a function $y(\mathbf{x})$ that distributes points in $\mathbf{x}$ according to the probability $\psi^2(\mathbf{x})$

$$y(\mathbf{x}) = \int_{-\infty}^{x} \psi^2(\tilde{\mathbf{x}})d\tilde{\mathbf{x}} \qquad 0 \le y(\mathbf{x}) \le 1$$

- The randomly generated points $0 \le y_i(\mathbf{x}) \le 1$ gives $\{\mathbf{x}_i\}$ that are distributed such that the density of points is $\psi^2(\mathbf{x})$.



$$\int A(\mathbf{x})\psi^2(\mathbf{x})d\mathbf{x} = \int_0^1 A(\mathbf{x})dy \approx \frac{1}{N}\sum_{i=1}^{N} A(\mathbf{x}_i)$$

- The statistical error in the $3n$-dimensional integration decreases as $N^{1/2}$ with the number of points N.
- The cost of MC integration is practically independent of n.
- The cost of VMC scales as n^3, which is due to determinant evaluations for computing $\psi(\mathbf{x})$ and $E_L(\mathbf{x})$.
- But, we require efficient methods for generating a set of points distributed as $\psi^2(\mathbf{x})$. → Metropolis sampling

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Metropolis sampling

- In the Metropolis method a *walker* samples the configuration space efficiently by means of a *random walk*.
  - Randomly select the direction of a step $\mathbf{x} \to \mathbf{x}'$
  - If the ratio $\psi^2(\mathbf{x}')/\psi^2(\mathbf{x})$ is larger than a random number between 0 and 1, then the step is taken.
  - Else, the walker does not move this time.
- In this way the points covered (*sampled*) by the walker are distributed according to $\psi^2(\mathbf{x})$.
- The Metropolis sampling can be made more efficient through using a type of *importance sampling*.
- Introduce a *transition probability* $T(\mathbf{x} \to \mathbf{x}')$ that favours steps in the direction of increasing $\psi^2(\mathbf{x})$.
- A step is accepted or rejected if a random number between 0 and 1 is less or greater than

$$\min\left(1, \frac{\psi^2(\mathbf{x}')}{\psi^2(\mathbf{x})}\frac{T(\mathbf{x} \to \mathbf{x}')}{T(\mathbf{x}' \to \mathbf{x})}\right)$$

Trial wave function optimization

- Having obtained a set of points $\{\mathbf{x}_i\}$ distributed as $\psi_T^2(\mathbf{x})$ for a given trial wave function, the energy may be evaluated

$$\langle E_T \rangle = \frac{1}{N} \sum_{i=1}^{N} \frac{\hat{H}\psi_T(\mathbf{x}_i)}{\psi_T(\mathbf{x}_i)} = \frac{1}{N} \sum_{i=1}^{N} E_L(\mathbf{x}_i)$$

- The energy of a new $\psi_{T'}(\mathbf{x})$ with slightly different orbital and correlation parameters may be estimated using the original points and reweighting

$$\langle E_{T'} \rangle = \frac{\sum_{i=1}^{N} w_i^2 \frac{\hat{H}\psi_{T'}(\mathbf{x}_i)}{\psi_{T'}(\mathbf{x}_i)}}{\sum_{i=1}^{N} w_i^2} \qquad w_i = \frac{\psi_{T'}(\mathbf{x})}{\psi_T(\mathbf{x})}$$

- It is then possible to optimize the nonlinear parameters without generating a new distribution for every new $\psi_{T'}(\mathbf{x})$.
- E is an upper bound to the exact energy, but has an attached statistical error, which is reduced at extra cost.

Diffusion Monte Carlo

- In VMC the Metropolis method is used to sample the distribution $\psi_T^2(\mathbf{x})$, where the form of $\psi_T(\mathbf{x})$ is known.
- In DMC the Metropolis method is used to sample the exact wave function directly.
- Consider the time dependent Schrödinger equation

$$i\frac{\partial \Psi}{\partial t}(\mathbf{x}, t) = \hat{H}\Psi(\mathbf{x}, t)$$

- The formal time dependent solutions are

$$\Psi(\mathbf{x}, t) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{x}) \exp(-iE_n t) \qquad \hat{H}\psi_n(\mathbf{x}) = E_n \psi_n(\mathbf{x})$$

- A general $\Psi(\mathbf{x}, t)$ can be expressed as a sum of the time independent eigenstates, which rotate in the complex plane with a frequency proportional to E_n.

- If we transform to *imaginary time* $\tau = it$ then

$$\frac{\partial \Psi}{\partial \tau}(\mathbf{x}, \tau) = -\hat{H}\Psi(\mathbf{x}, \tau) \qquad \Psi(\mathbf{x}, \tau) = \sum_{n=0}^{\infty} c_n \psi_n(\mathbf{x}) \exp(-E_n \tau)$$

- As $\Psi(\mathbf{x}, \tau)$ propagates in imaginary time the states all decay exponentially. Since the excited states decay faster than the ground state, $\Psi(\mathbf{x}, \tau)$ collapses to the ground state!

Compare

$$\frac{\partial \Psi}{\partial \tau}(\mathbf{x}, \tau) = \frac{1}{2}\nabla^2 \Psi(\mathbf{x}, \tau) - V(\mathbf{x})\Psi(\mathbf{x}, \tau) \qquad (1)$$

$$\frac{\partial C}{\partial t}(\mathbf{x}, t) = D\nabla^2 C(\mathbf{x}, t) - kC(\mathbf{x}, t) \qquad (2)$$

- The SE (1) is similar to the diffusion equation of a species undergoing a first order reaction (2).
    - $\Psi(\mathbf{x}, \tau)$ is equivalent to the concentration of the species.
    - $V(\mathbf{x})$ determines whether the concentration is increasing or decreasing at each point $\mathbf{x}$.

Metropolis sampling in DMC

The evolution of $\Psi(\mathbf{x}, \tau)$ to the exact GS via the diffusion equation is simulated by representing $\Psi(\mathbf{x}, \tau)$ as a *population* of walkers.

- Initialize the population (e.g. $\{\mathbf{x}_i\}$ from a VMC calculation)
- Move each walker by one time step $\Delta\tau$ in a random direction.
- At the new position each walker can *give birth* to a new walker, or *die*, or just exist, depending on the sign of the potential and a probability, given by a random number.
    - $V(\mathbf{x})$ negative → gives birth with probability $-V\Delta\tau$
    - $V(\mathbf{x})$ positive → dies with probability $V\Delta\tau$
- After long enough τ the population of walkers reaches a steady state, representing the exact $\psi_0(\mathbf{x})$

Importance sampling

- The convergence of DMC can be significantly accelerated by using a good trial $\psi_T(\mathbf{x})$ to *guide* the walkers.
- We define a function $f(\mathbf{x},\tau) = \psi_T(\mathbf{x})\Psi(\mathbf{x},\tau)$ and propagate $f(\mathbf{x},\tau)$ according to

  $$\frac{\partial f}{\partial \tau}(\mathbf{x},\tau) = \frac{1}{2}\nabla^2 f(\mathbf{x},\tau) - \frac{1}{2}\nabla \cdot [\nabla \ln \psi_T(\mathbf{x}) f(\mathbf{x},\tau)] - E_L(\mathbf{x}) f(\mathbf{x},\tau)$$

- This equation represents diffusion, drift and first order reaction.
- At large τ, $f(\mathbf{x},\tau) \to \psi_T(\mathbf{x})\psi_0(\mathbf{x}) \exp(-E_0\tau)$
- This method introduces two improvements
  - The drift term guides the walkers to regions where $\psi_0(\mathbf{x})$ is large, accelerating the convergence.
  - The birth and death rate now depends on the slowly varying local energy E_L, which is much easier to handle in a computation.
- The energy is evaluated by averaging the local energy over f.

The fixed node approximation

- The antisymmetry requirement for fermions means that there are nodes in the wave function.
- The direct application of DMC as described above leads to the bosonic state where there are no nodes.
- This is avoided by fixing the nodes of $\Psi(\mathbf{x},\tau)$ to be those of a good $\psi_T(\mathbf{x})$ - usually computed using VMC.
- The nodes partition the space and DMC is performed in each volume separately.
- This *fixed node* approximation introduces an error and the DMC energy is an upper bound.
- It is possible to release the nodes, allowing positive and negative walkers to meet and cancel each other. This method is currently inefficient and limited to small systems.

Illustrative calculations: small molecules

- FN-DMC and CCSD(T)/cc-pVTZ total energies (E_h).

Molecule	FN-DMC	CCSD(T)
CH_4	-40.5005(3)	-40.4381
NH_3	-56.5485(4)	-56.4732
C_2H_2	-77.3110(4)	-77.1876
C_2H_4	-78.5644(3)	-78.4388
H_2CO	-114.4739(4)	-114.3338
H_2O_2	-151.5213(3)	-151.3586
F_2	-199.4841(4)	-199.2961
O_3	-225.3410(4)	-225.1326

- The parentheses give the statistical errors. The error due to the fixed node approximation can be as much as 10%
- Note: errors are less systematic for DMC than CCSD(T).
- Note that CCSD(T) scales as n^7, compared to n^3 for DMC.

Illustrative calculations: C_{20} isomers

Isomer	FN-DMC	CCSD(T)
Ring	1.0	1.7
Bowl	0.0	0.0
Cage	2.0	0.0

- The ring bowl and cage isomers are very close in energy.
- The system is at the limit of the capability of CCSD(T).
- It is possible to provide reliable energy differences (eV) using QMC.

Concluding remarks

Method	Scaling	Accuracy	Max. size
FCI	$n!$	mE$_h$	2 atoms
CCSD(T)	n^7	mE$_h$	10-20 atoms
ECGs	$n!$	nE$_h$	4 electrons
GTGs	n^5, n^6	μE$_h$	10-20 electrons
R12	n^5, n^6, n^7	0.1-1 mE$_h$	10-20 atoms
QMC	n^3	10% E$_{\text{corr}}$	250-500 atoms