Anisotropic electron-pair densities in QMC

Manolo Per

RMIT University, Melbourne

August 1, 2008

3

ка Бък













Definitions

$$P(\mathbf{r}_{1},\mathbf{r}_{2}) = \frac{N(N-1)}{2} \int \Psi^{2}(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},\ldots,\mathbf{r}_{N}) d\mathbf{r}_{3},\ldots,d\mathbf{r}_{N}$$
(1)

- Full electron-pair density P(r₁, r₂) is a 6D quantity. Hard to visualize and interpret.
- 3D reductions to Intracule density *I*(**u**) and Extracule density *E*(**R**) retain 2-particle information.

Definitions

- Intracule refers to relative separation : $\mathbf{r}_{ij} = \mathbf{r}_i \mathbf{r}_j$.
- Extracule refers to centre-of-mass : $\mathbf{R}_{ij} = \frac{1}{2}(\mathbf{r}_i + \mathbf{r}_j)$.



(2)

 Investigate electronic structure using more info than density, without resorting to orbitals.

- Investigate electronic structure using more info than density, without resorting to orbitals.
- Coulson defined the Coulomb hole: *I_{exact} I_{UHF}*. Gives information on electron correlation effects.

- Investigate electronic structure using more info than density, without resorting to orbitals.
- Coulson defined the Coulomb hole: *I_{exact} I_{UHF}*. Gives information on electron correlation effects.
- Ab initio codes: QChem. Lots of four-centre integrals contracted with density matrices.

- Investigate electronic structure using more info than density, without resorting to orbitals.
- Coulson defined the Coulomb hole: *I_{exact} I_{UHF}*. Gives information on electron correlation effects.
- Ab initio codes: QChem. Lots of four-centre integrals contracted with density matrices.
- Requires accurate wavefunctions (e.g. Cl). QMC may be preferable for larger systems.

- Investigate electronic structure using more info than density, without resorting to orbitals.
- Coulson defined the Coulomb hole: *I_{exact} I_{UHF}*. Gives information on electron correlation effects.
- Ab initio codes: QChem. Lots of four-centre integrals contracted with density matrices.
- Requires accurate wavefunctions (e.g. Cl). QMC may be preferable for larger systems.
- Coulomb holes in DFT Work of Gori-Giorgi and coworkers.

Evaluating Densities

Densities in QMC usually evaluated using binning techniques.



- Smaller bins lead to larger variances.
- Regions of low density have large errors.
- Not smooth.

 Assaraf, Caffarel and Scemema¹ developed efficient estimator for the one-body density,

$$n(\mathbf{r}) = \sum_{i} \langle \delta(\mathbf{r} - \mathbf{r}_{i}) \rangle$$
(3)

²J.Toulouse,R.Assaraf, C.Umrigar, J. Chem. Phys **126** 244112 (2007)

¹R.Assaraf, M.Caffarel, A.Scemema, PRE **75** 035701 (2007)

 Assaraf, Caffarel and Scemema¹ developed efficient estimator for the one-body density,

$$n(\mathbf{r}) = \sum_{i} \langle \delta(\mathbf{r} - \mathbf{r}_{i}) \rangle$$
(3)

 Toulouse, Assaraf and Umrigar ² developed efficient estimators for spherically averaged Intracule density,

$$I(u) = (4\pi)^{-1} \int I(\mathbf{u}) d\Omega$$
 (4)

¹R.Assaraf, M.Caffarel, A.Scemema, PRE **75** 035701 (2007)

²J.Toulouse,R.Assaraf, C.Umrigar, J. Chem. Phys **126** 244112 (2007)

 Assaraf, Caffarel and Scemema¹ developed efficient estimator for the one-body density,

$$n(\mathbf{r}) = \sum_{i} \langle \delta(\mathbf{r} - \mathbf{r}_{i}) \rangle$$
(3)

 Toulouse, Assaraf and Umrigar ² developed efficient estimators for spherically averaged Intracule density,

$$I(u) = (4\pi)^{-1} \int I(\mathbf{u}) d\Omega$$
 (4)

 Benefit of low-variance estimators in QMC is the ability to calculate small differences accurately - Correlation effects in vdW systems accessible.

¹R.Assaraf, M.Caffarel, A.Scemema, PRE **75** 035701 (2007)

²J.Toulouse,R.Assaraf, C.Umrigar, J. Chem. Phys **126** 244112 (2007) + <= >

 Assaraf, Caffarel and Scemema¹ developed efficient estimator for the one-body density,

$$n(\mathbf{r}) = \sum_{i} \langle \delta(\mathbf{r} - \mathbf{r}_{i}) \rangle$$
(3)

 Toulouse, Assaraf and Umrigar ² developed efficient estimators for spherically averaged Intracule density,

$$I(u) = (4\pi)^{-1} \int I(\mathbf{u}) d\Omega$$
(4)

- Benefit of low-variance estimators in QMC is the ability to calculate small differences accurately - Correlation effects in vdW systems accessible.
- Key to both (sort of) is the idea of Zero-Variance Zero-Bias.

²J.Toulouse, R.Assaraf, C.Umrigar, J. Chem. Phys **126** 244112 (2007) • < = •

Manolo Per (RMIT University, Melbourne) Anisotro

Anisotropic electron-pair densities in QMC

¹R.Assaraf, M.Caffarel, A.Scemema, PRE **75** 035701 (2007)

R.Assaraf and M.Caffarel, J. Chem. Phys **119** 10536 (2003). To estimate $\langle \hat{O} \rangle$:

• Define Hamiltonian $\hat{H}^{\lambda} = \hat{H} + \lambda \hat{O}$, and exact wavefunction $\Psi_0^{\lambda} = \Psi_0 + \lambda \Psi_0'$ so exact energy is

$$E_{0}^{\lambda} = \left\langle E_{L,0}^{\lambda} \right\rangle_{\Psi_{0}^{\lambda 2}} = \frac{\langle \Psi_{0}^{\lambda} | \hat{H}^{\lambda} | \Psi_{0}^{\lambda} \rangle}{\langle \Psi_{0}^{\lambda} | \Psi_{0}^{\lambda} \rangle}$$
(5)

R.Assaraf and M.Caffarel, J. Chem. Phys **119** 10536 (2003). To estimate $\langle \hat{O} \rangle$:

• Define Hamiltonian $\hat{H}^{\lambda} = \hat{H} + \lambda \hat{O}$, and exact wavefunction $\Psi_0^{\lambda} = \Psi_0 + \lambda \Psi_0'$ so exact energy is

$$E_0^{\lambda} = \left\langle E_{L,0}^{\lambda} \right\rangle_{\Psi_0^{\lambda 2}} = \frac{\left\langle \Psi_0^{\lambda} | \hat{H}^{\lambda} | \Psi_0^{\lambda} \right\rangle}{\left\langle \Psi_0^{\lambda} | \Psi_0^{\lambda} \right\rangle} \tag{5}$$

• By Hellmann-Feynman, exact $O_0 = dE_0^{\lambda}/d\lambda|_{\lambda=0}$

R.Assaraf and M.Caffarel, J. Chem. Phys **119** 10536 (2003). To estimate $\langle \hat{O} \rangle$:

• Define Hamiltonian $\hat{H}^{\lambda} = \hat{H} + \lambda \hat{O}$, and exact wavefunction $\Psi_0^{\lambda} = \Psi_0 + \lambda \Psi_0'$ so exact energy is

$$E_{0}^{\lambda} = \left\langle E_{L,0}^{\lambda} \right\rangle_{\Psi_{0}^{\lambda 2}} = \frac{\langle \Psi_{0}^{\lambda} | \hat{H}^{\lambda} | \Psi_{0}^{\lambda} \rangle}{\langle \Psi_{0}^{\lambda} | \Psi_{0}^{\lambda} \rangle}$$
(5)

- By Hellmann-Feynman, exact $O_0 = dE_0^{\lambda}/d\lambda|_{\lambda=0}$
- Follow same procedure for approximate $\Psi^{\lambda} = \Psi + \lambda \Psi'$, obtain

$$dE^{\lambda}/d\lambda|_{\lambda=0} = \langle O_L \rangle_{\Psi^2} + \left\langle \left(\frac{\hat{H}\Psi'}{\Psi'} - E_L\right)\frac{\Psi'}{\Psi}\right\rangle_{\Psi^2} + 2\left\langle (E_L - E)\frac{\Psi'}{\Psi}\right\rangle_{\Psi^2} \\ = \langle O_L^{ZVZB} \rangle_{\Psi^2}$$
(6)

• For observables which do not commute with \hat{H} ,

$$\begin{split} \delta \langle O_L \rangle &= O(|\delta \Psi|) \\ \sigma^2(O_L) &= O(1) \end{split} \tag{7}$$

• For observables which do not commute with \hat{H} ,

$$\begin{split} \delta \langle O_L \rangle &= O(|\delta \Psi|) \\ \sigma^2(O_L) &= O(1) \end{split} \tag{7}$$

But for the new estimator,

$$\begin{split} \delta \langle O_L^{ZVZB} \rangle &= O(|\delta \Psi|^2 + |\delta \Psi| |\delta \Psi'|) \\ \sigma^2(O_L^{ZVZB}) &= O(|\delta \Psi|^2 + |\delta \Psi'|^2 + |\delta \Psi| |\delta \Psi'|) \end{split} \tag{8}$$

ZVZB Recipe

Modify local estimator

$$O_L^{ZVZB} = O_L + \Delta O_L^{ZV} + \Delta O_L^{ZB}$$

Define $Q = \Psi'/\Psi$.

(9)

ZVZB Recipe

Modify local estimator

$$O_L^{ZVZB} = O_L + \Delta O_L^{ZV} + \Delta O_L^{ZB}$$
(9)

Define $Q = \Psi'/\Psi$.

Zero-Variance term:

$$\Delta O_L^{ZV} = -\frac{1}{2} \left(\sum_k \nabla_k^2 \mathbf{Q} + 2\mathbf{v}_i \cdot \nabla_k \mathbf{Q} \right)$$
(10)

3

ト く 臣 ト く

ZVZB Recipe

Modify local estimator

$$O_L^{ZVZB} = O_L + \Delta O_L^{ZV} + \Delta O_L^{ZB}$$
(9)

Define $Q = \Psi'/\Psi$.

Zero-Variance term:

$$\Delta O_L^{ZV} = -\frac{1}{2} \left(\sum_k \nabla_k^2 \mathbf{Q} + 2\mathbf{v}_i \cdot \nabla_k \mathbf{Q} \right)$$
(10)

Zero-Bias term:

$$\Delta O_L^{ZB} = 2 \left(E_L - \langle E_L \rangle \right) Q \tag{11}$$

- Choose Q such that ∇²Q term in ZV correction cancels delta-function in original estimator.
- Use generalised identity:

$$g(\mathbf{r}_{ij},\mathbf{u})\nabla_{ij}^{2}\frac{1}{|\mathbf{r}_{ij}-\mathbf{u}|} = -4\pi\delta(\mathbf{r}_{ij}-\mathbf{u})$$
(12)

where $g(\mathbf{r}_{ij}, \mathbf{u} = \mathbf{r}_{ij}) = 1$.

- Choose Q such that ∇²Q term in ZV correction cancels delta-function in original estimator.
- Use generalised identity:

$$g(\mathbf{r}_{ij},\mathbf{u})\nabla_{ij}^{2}\frac{1}{|\mathbf{r}_{ij}-\mathbf{u}|} = -4\pi\delta(\mathbf{r}_{ij}-\mathbf{u})$$
(12)

where $g(\mathbf{r}_{ij}, \mathbf{u} = \mathbf{r}_{ij}) = 1$.

Suitable choice for spherically averaged intracule is

$$Q = -\frac{1}{8\pi} \sum_{i \neq j} \int \frac{g(\mathbf{r}_{ij}, \mathbf{u})}{|\mathbf{r}_{ij} - \mathbf{u}|} \frac{d\Omega_u}{4\pi}$$
(13)

- Choose Q such that ∇²Q term in ZV correction cancels delta-function in original estimator.
- Use generalised identity:

$$g(\mathbf{r}_{ij},\mathbf{u})\nabla_{ij}^{2}\frac{1}{|\mathbf{r}_{ij}-\mathbf{u}|} = -4\pi\delta(\mathbf{r}_{ij}-\mathbf{u})$$
(12)

where $g(\mathbf{r}_{ij}, \mathbf{u} = \mathbf{r}_{ij}) = 1$.

Suitable choice for spherically averaged intracule is

$$Q = -\frac{1}{8\pi} \sum_{i \neq j} \int \frac{g(\mathbf{r}_{ij}, \mathbf{u})}{|\mathbf{r}_{ij} - \mathbf{u}|} \frac{d\Omega_u}{4\pi}$$
(13)

g chosen to give correct asymptotic behaviour

$$g(\mathbf{r}_{ij},\mathbf{u}) = e^{-\alpha|\mathbf{r}_{ij}-\mathbf{u}|}$$
(14)

Leads to the expressions

$$I^{ZV}(u) = -\frac{1}{4\pi} \sum_{i \neq j} \left[\mathbf{v}_i \cdot \frac{\mathbf{r}_{ij}}{r_{ij}^2} \left(A(r_{ij}, u) + \frac{1}{u} B(r_{ij}, u) \right) - \frac{\alpha^2}{2} A(r_{ij}, u) \right]$$
(15)
$$\Delta I^{ZB}(u) = -\frac{1}{4\pi} (E_L - E) \sum_{i \neq j} A(r_{ij}, u)$$
(16)

where A, B are simple functions of exponentials.

• Low variance, smooth, and can sample regions where electrons never go.

A Note on Zero-Bias



A Note on Zero-Bias



Spherical Coulomb hole in He₂



Spherical Coulomb hole in He₂



Anisotropic Intracule and Extracule Densities

- As a tool for understanding molecular electronic structure, spherical average washes out lots of information.
- Anisotropic intracule and extracule densities tell us about electron-pair orientation.
- Can we simply use the approach of Toulouse *et al. without* performing the spherical average?
- Choose Q so that $\nabla_k^2 Q$ term cancels delta-function.
- Suitable choice is

$$Q = -\frac{1}{8\pi} \sum_{i \neq j} \frac{g(\mathbf{r}_{ij}, \mathbf{u})}{|\mathbf{r}_{ij} - \mathbf{u}|}$$
(17)

Intracule Density

Plugging Q into ZV expression gives

$$\begin{split} \mathcal{I}^{ZV}(\mathbf{u}) &= \frac{1}{8\pi} \sum_{i \neq j} \left[\frac{\alpha^2}{|\mathbf{r}_{ij} - \mathbf{u}|} e^{-\alpha |\mathbf{r}_{ij} - \mathbf{u}|} + \frac{e^{-\alpha |\mathbf{r}_{ij} - \mathbf{u}|}}{|\mathbf{r}_{ij} - \mathbf{u}|^2} \mathbf{v}_i \cdot (\mathbf{r}_{ij} - \mathbf{u}) \left(\frac{1}{|\mathbf{r}_{ij} - \mathbf{u}|} - \alpha \right) \right. \\ &+ \frac{e^{-\alpha |\mathbf{r}_{ij} - \mathbf{u}|}}{|\mathbf{r}_{ji} - \mathbf{u}|^2} \mathbf{v}_i \cdot (\mathbf{r}_{ji} - \mathbf{u}) \left(\frac{1}{|\mathbf{r}_{ji} - \mathbf{u}|} - \alpha \right) \right] \end{split}$$

• This ZV estimator has unpredictable error bars.

Behaviour of First ZV Estimator



August 1, 2008 19 / 41

Intracule Densities

- Averaging this expression to get the spherical intracule removes nasty behaviour.
- In 3D, we can obtain a well-behaved estimator by considering the complete expectation value of *I^{ZV}*,

$$\int \Psi_T^2 h^{ZV}(\mathbf{u}) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$$
(18)

and performing an integration by parts on the troublesome terms. Requires representation in terms of single-particle derivatives.

Equivalent estimator is

$$I^{ZV}(\mathbf{u}) = -\frac{1}{8\pi} \sum_{i \neq j} \left\{ \left(\frac{\nabla_i^2 \Psi}{\Psi} + \mathbf{v}_i \cdot \mathbf{v}_i \right) \left[\frac{e^{-\alpha |\mathbf{r}_{ij} - \mathbf{u}|}}{|\mathbf{r}_{ij} - \mathbf{u}|} + \frac{e^{-\alpha |\mathbf{r}_{ij} - \mathbf{u}|}}{|\mathbf{r}_{ji} - \mathbf{u}|} \right] - \frac{\alpha^2}{|\mathbf{r}_{ij} - \mathbf{u}|} e^{-\alpha |\mathbf{r}_{ij} - \mathbf{u}|} \right\}$$
(19)

٠

Behaviour of Both ZV Intracule Estimators



Linear Molecules

- Cylindrical coordinates (ρ, ϕ, z) . Align molecule along z-axis.
- Cylindrical symmetry, so $I(\mathbf{u})$ and $E(\mathbf{R})$ reduce to 2D quantities.
- To retain probabilistic interpretation,

$$F(\rho, z) = 2\pi \rho I(\rho, z) \tag{20}$$

 Prob. of finding electron pair a distance z apart along the bond, and simultaneously a distance p apart perpendicular to the bond.

Interpretation: RHF H₂, R = 12.0 a.u.





Manolo Per (RMIT University, Melbourne)

Anisotropic electron-pair densities in QMC

Application to Stretched H₂ molecule

 Rassolov *et al.* ³ noticed interesting behaviour in the correlation energy of H₂ centered at around r = 2.5 a.u.



Manolo Per (RMIT University, Melbourne) Ar

Hartree-Fock Basis and Trial Wavefunction

- Optimized Gaussian basis of 20s11p6d. E_{HF} within 1 × 10⁻⁷ Hartree of HF limit.
- Usual DTN Jastrow ⁴ not as good as expected for H₂. At equilibrium geometry gives -1.17353(1) Ha compared to accurate value of -1.174475 Ha.
- DTN Jastrow includes EE, EN, EEN correlation.



⁴N.D.Drummond, M.D.Towler, R.J.Needs, PRB **70** 235119 (2004)

Hartree-Fock Basis and Trial Wavefunction

- Wavefunction of Alexander+Coldwell ⁵ can be written in Slater-Jastrow form. Slater part is product of 1s Slaters orbitals.
- This ENEN Jastrow fully correlates electron-pairs and nuclei in scaled coordinates:

$$J_{ij}^{AB} = \sum_{Imnpq} \gamma_{Imnpq}^{AB} \tilde{r}_{iA}^{I} \tilde{r}_{jA}^{m} \tilde{r}_{iB}^{n} \tilde{r}_{jB}^{p} \tilde{r}_{ij}^{q}$$
(21)

where scaled coordinates are

$$\tilde{r} = r/(1+\alpha r) \tag{22}$$

and $I + m + n + p + q \leq N$.



⁵S.A.Alexander and R.L.Coldwell, J. Chem. Phys **121** 11557 (2004)

Wavefunction Quality

Table: VMC Energies (in Ha) of H₂

Bond Length (a.u.)	DTN(14;14;4,4)	AC(N=6)	KW ⁶
1.4	-1.17353(1)	-1.1744756(7)	-1.1744744
2.0	-1.13374(2)	-1.1381318(8)	-1.1381312
2.5	-1.06481(3)	-1.093936(2)	-1.0939273
3.0	-1.02422(3)	-1.057317(2)	-1.0573118

Quality of DTN Jastrow decreases as nuclei pulled apart. ENEN correlation important here.

⁶W.Kolos and L.Wolniewicz, J. Chem. Phys **43** 2429 (1965) ィロトィタト イミト イミト ミーク

Possibly interesting quantities

- Average interparticle distance, $\langle r_{ij} \rangle$.
- Spherically averaged intra/extracule densities I(u), E(R), and correlation shifts.
- Full 2D intra/extracule densities and correlation shifts.

Spherically-averaged Intracule Density, R = 1.4 a.u.



Spherically-averaged Intracule Density, R = 2.0 a.u.



Spherically-averaged Intracule Density, R = 2.5 a.u.



Spherically-averaged Intracule Density, R = 3.0 a.u.



Manolo Per (RMIT University, Melbourne) Anisotropic electron-pair densities in QMC

August 1, 2008 32 / 41

Anisotropic Intracule Density, R=1.4 a.u.

Figure: Contours at 0.115,0.08,0.02



Anisotropic Intracule Density, R=2.0 a.u.

Figure: Contours at 0.075,0.05,0.02



Anisotropic Intracule Density, R=2.5 a.u.

Figure: Contours at 0.062,0.04,0.02



Anisotropic Intracule Density, R=3.0 a.u.

Figure: Contours at 0.06,0.04,0.02



Interpretation

- Anisotropic intracule density clearly shows the strong effect of correlation in the region 2.0 – 3.0.
- Uncorrelated electrons lead to a delocalisation of the intracule density around R = 2.5, but with the peak at z = 0.
- Correlation reduces the chance of finding electrons at small relative z.
- UHF too ionic in this region, doesn't want to dissociate cleanly.

• Extension to consider bonding properties is also possible. Recently done for spherically-averaged properties of atoms in molecules by Ugalde.

- Extension to consider bonding properties is also possible. Recently done for spherically-averaged properties of atoms in molecules by Ugalde.
- In QMC we can consider the binding of arbitrary fragments.

$$\Delta I(\mathbf{r}) = I_{int}(\mathbf{r}) - I_{non-int}(\mathbf{r})$$
(23)

- Extension to consider bonding properties is also possible. Recently done for spherically-averaged properties of atoms in molecules by Ugalde.
- In QMC we can consider the binding of arbitrary fragments.

$$\Delta I(\mathbf{r}) = I_{int}(\mathbf{r}) - I_{non-int}(\mathbf{r})$$
(23)

One-body densities are easy. Consider two fragments, A and B.

$$n_{non-int}(\mathbf{r}) = n_A(\mathbf{r}) + n_B(\mathbf{r})$$
(24)

 Pair densities are more complicated, can't simply add values from isolated fragments.

- Pair densities are more complicated, can't simply add values from isolated fragments.
- Wavefunction for non-interacting fragments is $\Psi_A \Psi_B$. We need the intracule density according to this distribution.

- Pair densities are more complicated, can't simply add values from isolated fragments.
- Wavefunction for non-interacting fragments is $\Psi_A \Psi_B$. We need the intracule density according to this distribution.
- As well as the contribution from intracules from systems *A* and *B*, we will need cross terms:

$$\frac{1}{2} \sum_{i \in A} \sum_{j \in B} \frac{\langle \Psi_A \Psi_B | \delta(\mathbf{r}_{ij} - \mathbf{u}) | \Psi_A \Psi_B \rangle}{\langle \Psi_A^2 \Psi_B^2 \rangle}$$
(25)

- Pair densities are more complicated, can't simply add values from isolated fragments.
- Wavefunction for non-interacting fragments is $\Psi_A \Psi_B$. We need the intracule density according to this distribution.
- As well as the contribution from intracules from systems *A* and *B*, we will need cross terms:

$$\frac{1}{2} \sum_{i \in A} \sum_{j \in B} \frac{\langle \Psi_A \Psi_B | \delta(\mathbf{r}_{ij} - \mathbf{u}) | \Psi_A \Psi_B \rangle}{\langle \Psi_A^2 \Psi_B^2 \rangle}$$
(25)

A full OO QMC code would be nice!

Summary

- ZB correction not that useful for realistic simple trial wavefunctions.
- Preliminary work on He₂ shows different behaviour of I(u) than FCI result around u = 5.6. Real or Ψ_T artefact?
- Derived ZVZB expressions for the full 3D Intracule and Extracule densities.
- Application to stretched H₂ helps explain increased importance of correlation as molecule dissociates.
- Possibility of using QMC to discover more about detailed interactions between fragments.

Acknowledgements

- Prof. Ian Snook, A.Prof Salvy Russo.
- Australian Research Council