

Explicitly correlated wavefunctions

Chris Chi, University of Chicago

Abstract

Orbital based electronic structure methods are widely used to compute properties of chemical systems and yield accurate results in systems without strong correlations, yet with the basis sets commonly used today, these exhibit slow convergence towards the complete basis set limit. This is partially due to the inability of commonly used basis sets, such as cc-pVXZ, to properly represent the correlation cusp condition with a finite number of contracted Gaussian basis elements. By including an explicitly addressing correlation cusp, these techniques can exhibit better convergence properties, but sometimes at the cost of additional computational resources required.

Theory

Cusp conditions

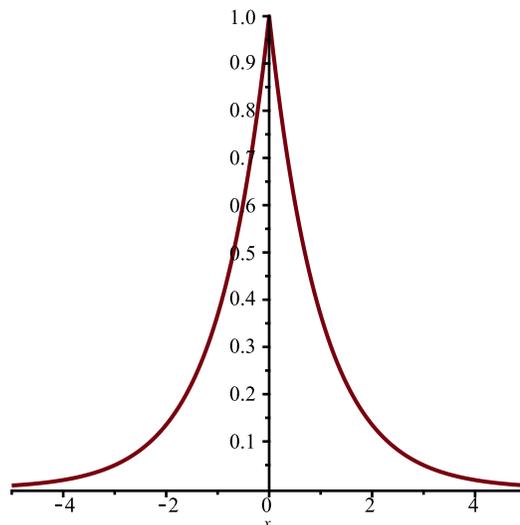
In the Born-Oppenheimer approximation, the ground state wavefunction of the Hydrogen atom has the form

$$\psi = e^{-|\mathbf{r}|}$$

which has a discontinuous first derivative at $|\mathbf{r}| = 0$ and satisfies

$$\left. \frac{d}{d|\mathbf{r}|} \psi \right|_{|\mathbf{r}|=0} = -\psi(0)$$

plot($e^{-|x|}$, $x = -5..5$)



It can be shown [1] that the wavefunction for a multi electron system similarly has a discontinuous first

derivative when $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = 0$, and that the derivative satisfies

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

The existence of these discontinuities cause the kinetic energy to diverge when the respective $r = 0$, compensating for the divergence of the potential energy such that the total energy is finite.

All orbital based electronic structure make at least two approximations: one that is intrinsic to the method itself, e.g. neglecting coulombic correlation terms in Hartree-Fock methods or neglecting higher order excitations in CISD, and another that results from the restriction of the resulting optimization problem to a finite dimensional subspace. By expanding the size of the space spanned by these finite bases, the result in the infinite basis set limit for a particular method can be extrapolated. The convergence properties of orbital based methods depend heavily, however, on the particular choice of basis. The basis elements of choice for most modern electronic structure packages are contracted Gaussian orbitals, which have the advantage of having simple, analytically computable integrals. However, contracted Gaussian atomic orbitals do not satisfy the nuclear cusp condition, and Slater determinants of contracted Gaussian atomic orbitals do not satisfy the electronic cusp conditions.

Hylleraas' explicitly correlated helium ground state

Hylleraas [2] proposed that the helium ground state orbital take the form

$$\psi = e^{-\alpha(|\mathbf{r}_1| + |\mathbf{r}_2|)} \left(1 - b|\mathbf{r}_1 - \mathbf{r}_2| \right)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and α and b are parameters to be variationally optimized. Due to the presence of r_{12} , the natural coordinates for the system are given by (s, t, u) , where

$$s = |\mathbf{r}_1| + |\mathbf{r}_2|$$

$$t = |\mathbf{r}_1| - |\mathbf{r}_2|$$

$$u = |\mathbf{r}_1 - \mathbf{r}_2|$$

In (s, t, u) coordinates, the proposed wavefunction has the form

$$\psi = (1 - bu)e^{-\alpha s}$$

Under the Born-Oppenheimer approximation, the Hamiltonian of the helium atom has form

$$H = \frac{\nabla_1^2}{2} + \frac{\nabla_2^2}{2} - \frac{1}{|\mathbf{r}_1|} - \frac{1}{|\mathbf{r}_2|} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

The approximate ground state energy can be obtained as

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

After performing the change of variables and necessary integrals, the energy as a function of α and b is

$$E = \frac{\alpha(2\alpha^2(-27 + 8\alpha) + 2b\alpha(-104 + 25\alpha) + b^2(-253 + 64\alpha))}{2(48b^2 + 35b\alpha + 8\alpha^2)}$$

Differentiating with respect to α and b , the minimum energy can be found to be $E = -2.89112$ at $\alpha = 1.84968$, $b = 0.365796$.

R12 methods

A generalization [3] of Hylleraas' method to larger systems can be obtained using the ansatz

$$\psi = g\Phi,$$

where Φ is a function such that $\nabla\Phi$ and $\nabla^2\Phi$ are both continuous. Φ cannot have an electronic cusp, and so the cusp in ψ must be introduced by g . The Schrodinger equation then gives

$$\begin{aligned} (H - E)\psi &= (K + T_{12} + V_{12} - E)g\Phi \\ &= (K - E)g\Phi + V_{12} + [T_{12}, g]\Phi + gT_{12}\Phi = 0, \end{aligned}$$

where T_{12} is the sum of the kinetic energy operators for electrons 1 and 2, V_{12} is the interaction potential between electrons 1 and 2, and K is everything else in the Hamiltonian. When $|\mathbf{r}_{12}| = 0$, the interaction potential V_{12} diverges, so for the Schrodinger equation to yield a finite energy, it must be that the other terms diverge in a way that compensate for the divergence of V_{12} . The term $gT_{12}\Phi$ is finite at $|\mathbf{r}_{12}| = 0$, as g must be a continuous function for ψ to be continuous, and T_{12} is a second order differential operator acting on Φ , which has continuous first and second derivatives. Thus it must be $[T_{12}, g]\Phi$ that diverges to compensate for V_{12} . This is satisfied for

$$g = 1 + \frac{1}{2}r_{12},$$

since

$$\begin{aligned} \left[T_{12}, \frac{|\mathbf{r}_{12}|}{2} \right] &= -\frac{1}{|\mathbf{r}_{12}|} - \frac{1}{2}\nabla_1|\mathbf{r}_{12}| \cdot \nabla_1 - \frac{1}{2}\nabla_2|\mathbf{r}_{12}| \cdot \nabla_2 \\ &= -\frac{1}{|\mathbf{r}_{12}|} - \frac{1}{2}\frac{(\mathbf{r}_1 - \mathbf{r}_2)}{|\mathbf{r}_{12}|}(\nabla_1 - \nabla_2) \\ &= -V_{12} + U_{12} \end{aligned}$$

so the V_{12} terms cancel. Repeating this for every pair of electrons gives

$$g = \prod_{i < j} \left(1 + \frac{1}{2}|\mathbf{r}_{ij}| \right).$$

Φ can then be expanded in a basis of Slater determinants.

Computational results

The result of Hylleraas' results for helium can be compared to numerical results obtained from a few different methods.

```
> Digits := 15 ;
with(QuantumChemistry);
molecule := [{"He", 0, 0, 0}];
```

Digits := 15

[*AOLabels, ActiveSpaceCI, ActiveSpaceSCF, AtomicData, BondAngles, BondDistances, Charges, ChargesPlot, CorrelationEnergy, CoupledCluster, DensityFunctional, DensityPlot3D, Dipole, DipolePlot, Energy, FullCI, GeometryOptimization, HartreeFock, Interactive, Isotopes, MOCoefficients, MODiagram, MOEnergies, MOIntegrals, MOOccupations, MOOccupationsPlot, MOSymmetries, MP2, MolecularData, MolecularGeometry, NuclearEnergy, NuclearGradient, Parametric2RDM, PlotMolecule, Populations, RDM1, RDM2, ReadXYZ, SaveXYZ, SearchBasisSets, SearchFunctionals, SkeletalStructure, Thermodynamics, Variational2RDM, VibrationalModeAnimation, VibrationalModes, Video*]

molecule := [{"He", 0, 0, 0}] **(3.1.1)**

Hartree-Fock

```
> Energy(molecule, method = HartreeFock, basis = "sto3g", symmetry = true);
-2.80778396 (3.2.1)
```

```
> Energy(molecule, method = HartreeFock, basis = "cc-pVDZ", symmetry = true);
-2.85516048 (3.2.2)
```

```
> Energy(molecule, method = HartreeFock, basis = "cc-pVTZ", symmetry = true);
-2.86115334 (3.2.3)
```

```
> Energy(molecule, method = HartreeFock, basis = "cc-pVQZ", symmetry = true);
-2.86151423 (3.2.4)
```

```
> Energy(molecule, method = HartreeFock, basis = "cc-pV5Z", symmetry = true);
-2.86162483 (3.2.5)
```

MP2

```
> Energy(molecule, method = MP2, basis = "cc-pVDZ", symmetry = true);
-2.88098882 (3.3.1)
```

```
> Energy(molecule, method = MP2, basis = "cc-pVTZ", symmetry = true);
-2.89429091 (3.3.2)
```

```
> Energy(molecule, method = MP2, basis = "cc-pVQZ", symmetry = true);
-2.89699223 (3.3.3)
```

```
> Energy(molecule, method = MP2, basis = "cc-pV5Z", symmetry = true);
-2.89803135 (3.3.4)
```

Full CI

```
> Energy(molecule, method = FullCI, basis = "cc-pVDZ", symmetry = true);
-2.88759483 (3.4.1)
```

```
> Energy(molecule, method = FullCI, basis = "cc-pVTZ", symmetry = true);
-2.90023217 (3.4.2)
```

```
> Energy(molecule, method = FullCI, basis = "cc-pVQZ", symmetry = true);
-2.90241088 (3.4.3)
```

```
> Energy(molecule, method = FullCI, basis = "cc-pV5Z", symmetry = true);
(3.4.4)
```

For comparison, the experimentally determined ground state energy of helium is -2.90338583 [4], and the energy computed by Hylleraas' method is -2.89112. Hartree-Fock completely neglects electron correlation energy other than the intrinsic fermionic nature of the Slater determinant wavefunction and has a higher computed ground state energy than the Hylleraas wavefunction, which accounts for electron correlation explicitly. Hylleraas' results are comparable even to post Hartree-Fock methods using rather large bases of contracted Gaussian orbitals.

References

- [1] Kato, T. On the Eigenfunctions of Many-Particle Systems in Quantum Mechanics. *Communications on Pure and Applied Mathematics* 1957, 10 (2), 151–177.
- [2] Hylleraas, E. A. Über Den Grundzustand Des Heliumatoms. *Zeitschrift für Physik* 1928, 48 (7-8), 469–494.
- [3] Kutzelnigg, W. r 12-Dependent Terms in the Wave Function as Closed Sums of Partial Wave Amplitudes for Large l. *Theoretica Chimica Acta* 1985, 68 (6), 445–469.
- [4] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team. "NIST Atomic Spectra Database Ionization Energies Data". Gaithersburg, MD: NIST.