A new Jastrow factor for CASINO

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Slater-Jastrow wavefunctions

- CASINO uses a *Slater-Jastrow* trial wavefunction:

$$\Psi = \exp(J) D^{\uparrow} D^{\downarrow}, \tag{1}$$

  where $D^{\uparrow}$ and $D^{\downarrow}$ are Slater determinants for spin-up and down electrons, and $\exp(J)$ is a *Jastrow factor*.

- J contains free parameters, to be determined by minimising the variance of the local energy.

- An S-J wavefunction can recover a large fraction of the correlation energy (the difference of the energy expectation with respect to the Slater determinants and the ground-state energy).

The need for a good Jastrow factor

- The DMC energy is, in principle, independent of the Jastrow factor.

- In practice, a poor wavefunction leads to larger statistical error bars, larger timestep biases, larger population control biases and more instability problems.

- A poor wavefunction also leads to errors resulting from the *locality approximation* in pseudopotential calculations.

- Quantities that do not commute with the Hamiltonian are evaluated using *extrapolated estimators*. These *do* depend on the Jastrow factor.

Requirements of a Jastrow factor

The Jastrow factor must:

1. Satisfy the *Kato cusp conditions*. (Otherwise the local energy will diverge.)

2. Be symmetric under electron exchanges.

3. Be twice differentiable, so that the kinetic-energy integrand is well-defined.

4. Be extremely quick to evaluate.

5. Be parametrised efficiently.

The Kato cusp conditions (1)

- The electron–electron cusp condition is:

$$\left(\frac{\partial\widehat{\Psi}}{\partial r_{ij}}\right)_{r_{ij}=0} = \Gamma_{ij}\,(\Psi)_{r_{ij}=0}\,, \qquad (2)$$

  where $\widehat{\Psi}$ is the spherical average of Ψ about the coalescence point of electrons i and j, and $\Gamma_{ij} = 1/2$ for antiparallel electrons and $1/2$ for parallel ones.

- $D^{\uparrow}$ and $D^{\downarrow}$ do not have electron–electron cusps. So J must satisfy

$$\left(\frac{\partial J}{\partial r_{ij}}\right)_{r_{ij}=0} = \Gamma_{ij}. \qquad (3)$$

The Kato cusp conditions (2)

- A similar cusp condition applies when an electron approaches a nucleus.

- This cusp condition *may* be satisfied by the orbitals.

- If the orbitals are cuspless at nuclei, J must satisfy:

$$\left(\frac{\partial J}{\partial r_{iI}}\right)_{r_{iI}=0} = -Z_I. \tag{4}$$

The new Jastrow factor

The Jastrow factor consists of 5 types of term:

1. Isotropic functions of electron–electron separations $u(r_{ij})$.

2. Isotropic functions of electron–ion separations $\chi(r_{iI})$.

3. Isotropic functions of electron–electron and electron–ion separations $f(r_i, r_j, r_{ij})$.

4. Plane-wave expansions in electron–electron separations $p(\mathbf{r}_{ij})$.

5. Plane-wave expansions in electron positions $q(\mathbf{r}_i)$.

The isotropic electron–electron term

- $u(r_{ij})$ is a polynomial; the polynomial coefficients are optimisable parameters.

- If $r_{ij} \geq L_u$ then $u(r_{ij}) = 0$. The cutoff length L_u is an optimisable parameter.

- A factor of $(r_{ij} - L_u)^C$ is included in u. C must be at least 2. If $C \geq 3$ then the local energy is continuous at the cutoff radius.

- The e–e cusp condition is used to eliminate one of the expansion coefficients.

- There may be different expansion coefficients for parallel and antiparallel spin pairs.

The isotropic electron–nucleus term

- χ is intended to "undo the effect of u on the HF charge density".

- $\chi(r_{iI})$ is a polynomial. There is a separate χ-function for each type of ion in the simulation.

- If $r_{iI} \geq L_\chi$ then $\chi(r_{iI}) = 0$. $\chi(r_{iI})$ includes a factor of $(r_{iI} - L_\chi)^C$.

- The χ-function is cuspless at nuclei if the orbitals satisfy the e–n cusp condition; otherwise χ must satisfy the cusp condition. In either case, one of the expansion coefficients is eliminated.

- Different expansion coefficients are allowed for different electron spins. (Useful in spin-polarised systems.)

The electron–electron–nucleus term

- $f(r_{iI}, r_{jI}, r_{ij})$ is an expansion in powers of r_{iI}, r_{jI} and r_{ij}. There is a separate f-function for each type of ion in the simulation.

- f must be symmetric under the exchange of electrons i and j.

- If $r_{iI} \geq L_f$ or $r_{jI} \geq L_f$ then $f = 0$. A factor of $(r_{iI} - L_f)^C (r_{jI} - L_f)^C$ is included in f.

- The no-cusp conditions give a set of linear equations involving the expansion coefficients. A subset of the coefficients can be expressed in terms of the others.

- f can include e–e terms that are like ion-specific u-functions.

The plane-wave expansions

- $p(\mathbf{r}_{ij})$ describes electron–electron correlation over the whole system; it therefore has the periodicity and symmetry of the simulation cell.

- $q(\mathbf{r}_i)$ repairs the charge density. It therefore has the periodicity and symmetry of the charge density.

- Both p and q are cuspless.

The new Jastrow factor in full

$$
\begin{aligned}
J(\mathbf{R}) \quad = \quad & \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}) + \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^{N} \chi_I(r_{iI}) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} p(\mathbf{r}_{ij}) \\
& + \sum_{I=1}^{N_{\text{ions}}} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} f_I(r_{iI}, r_{jI}, r_{ij}) + \sum_{i=1}^{N} q(\mathbf{r}_i) \qquad (5)
\end{aligned}
$$

where

$$u(r_{ij}) = (r_{ij} - L_u)^C \left(\alpha_0 + \left(\frac{\Gamma_{ij}}{(-L_u)^C} + \frac{\alpha_0 C}{L_u} \right) r_{ij} + \sum_{l=2}^{N_u} \alpha_l r_{ij}^l \right)$$

$$\chi_I(r_{iI}) = (r_{iI} - L_{\chi I})^C \left(\beta_{0I} + \left(\frac{-Z_I}{(-L_{\chi I})^C} + \frac{\beta_{0I} C}{L_{\chi I}} \right) r_{iI} + \sum_{m=2}^{N_\chi} \beta_{mI} r_{iI}^m \right)$$

$$f_I(r_{iI}, r_{jI}, r_{ij}) = \sum_{l=0}^{N_{fI}^{\text{eN}}} \sum_{m=0}^{N_{fI}^{\text{eN}}} \sum_{n=0}^{N_{fI}^{\text{ee}}} \gamma_{lmnI} r_{iI}^l r_{jI}^m r_{ij}^n (r_{iI} - L_{fI})^C (r_{jI} - L_{fI})^C$$

$$p(\mathbf{r}_{ij}) = \sum_A a_A \sum_{\mathbf{G}_A^S +} \cos(\mathbf{G}_A^S \cdot \mathbf{r}_{ij})$$

$$q(\mathbf{r}_i) = \sum_B b_B \sum_{\mathbf{G}_B^P +} \pm \cos(\mathbf{G}_B^P \cdot \mathbf{r}_i)$$

Helium atom investigation

- Using CASINO's old Jastrow factor, or using the new Jastrow with just the u- and χ-terms present, 91.7(7)% of the correlation energy can be retrieved.

- Using the new Jastrow with u, χ and f, 99.848(5)% of the correlation energy can be recovered.

- The f-terms are important in systems with bare nuclei.

Silane molecule investigation

- A silicon pseudopotential was used.
- The main problem with the old Jastrow is the inability to optimise the cutoff lengths.
- VMC, variance minimisation and DMC work just as well with $C = 2$ as with $C = 3$.
- The optimal expansion order is about 4 and the f-terms are of no use in this system.
- Optimising the cutoffs slows down the convergence in variance minimisation.
- The cutoff lengths, especially those of χ, are fairly independent of the expansion order. Optimise cutoffs at low orders!

Neon atom investigation (1)

All-electron neon, pseudoneon and a neon 8+ ion were studied. Here are some results:

System	**Jastrow**	**% corr. E (a.u.)**
Ne	Old	59(2)%
Ne	New	88.9(16)%
Ne (PSP)	Old	86.3(5)%
Ne (PSP)	New	95.7(4)%
Ne^{8+}	New	100.3(6)%

Results obtained using the new Jastrow without f were the same as the results obtained using the old Jastrow factor.

Neon atom investigation (2)

- The f-terms are far more important in neon than pseudoneon. However, one must either have a high expansion order or permit duplication of u by f. This is because of the different length-scales in neon.

- DMC timestep biasing is almost 10 times worse in neon than pseudoneon, even if f is used for neon and not used for pseudoneon. So pseudopotentials are still useful for simulations of large nuclei!

- Results so far suggest it is better to use orbitals which satisfy the e–n cusp condition and have cuspless χ-terms than *vice versa*.

Conclusions and further work

- A new form of Jastrow factor has been developed for CASINO. It performs better than the old form. We believe it is the most general and efficient Jastrow factor yet developed.

- Some further tests are required:

  1. Investigate silicon. Look at the behaviour of the cutoffs in a periodic system. Try using the p- and q-terms.

  2. (MDT) Investigate nickel oxide. Do the f-terms help here?

  3. Study various issues of computational efficiency in detail.