Pseudo-interactions and the electron-electron cusp

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Abstract

Within this contribution, we discuss a recent study [D. Prendergast, M. Nolan, C. Filippi, S. Fahy and J.C. Greer, Journal of Chemical Physics **115** 1626 (2001)] whereby the electron-electron interaction is replaced by a pseudo-interaction. The pseudo-interaction is chosen to eliminate electron-electron cusps in the many-body wavefunction, and we use this property to study the role of the cusp on convergence in configuration interaction (CI) calculations. Surprisingly, we find that the electron-electron cusp plays little role in determining CI energies, and for chemical accuracy, the slow convergence of CI calculations can not be attributed to fitting electron-electron cusps.

1 Introduction

In this short highlight, we discuss a method of modifying the Coulomb interaction for short electron-electron distances, while maintaining many-body eigenstate energies close to those of the true interaction, which could be expected to improve the convergence properties for configuration interaction (CI) expansions. The method is based on analogous ideas for treating electron-ion interactions with norm-conserving pseudopotentials in order to improve the convergence properties of plane-wave expansions for single-particle wavefunctions. We will show that a representation of the cusps in electronic structure theory turns out *not* to be critical to determination of electronic energies when required to "chemical accuracy" ($\approx$ 1 milliHartree): this result is contrary to commonly held assumptions within the electronic structure community.

The divergence of the $1/r$ electron-electron interaction in many-electron systems (all quantities in atomic units) produces an infinite potential energy at electron-electron coalescences. However, since an eigenstate ψ of the Hamiltonian H, with energy E, satisfies the Schrödinger equation, $H\psi = E\psi$, the local energy $(H\psi)/\psi = E$ at such coalescences does not diverge. This non-divergent local energy is guaranteed by the imposition of cusp conditions on the many-body wave function [1] where two electrons coincide, causing the infinite potential energy to be cancelled

by an equal and opposite divergence of the kinetic energy (the same phenomenon occurs for electron-nucleus interactions).

Configuration interaction calculations use an expansion in configuration state functions comprised of spin coupled sums of determinants built from single-particle orbitals. It has been stated that the expansion is slowly convergent because, being a smooth function of the separation between any two electrons, it cannot easily reproduce the required cusps in the wavefunction at electron-electron coalescences [2]. To avoid this difficulty, we replaced the divergent $1/r$ electron-electron interaction with an interaction that is smooth and finite at the origin [3]. Much to our surprise, we found this removal of the cusp made little difference to the convergence of CI expansions at the approximation level of a milliHartree per atom.

In the approach outlined here, we show how to keep the energy and the intermediate- and long-range correlation properties of the many-body eigenstate unchanged. In particular, our new (smooth) interaction should ideally have scattering properties identical to the true interaction for all energies. If this were the case, all many-electron eigenvalues would be identical for both interactions. While this is the ideal, we expect that a potential which gives the same scattering properties as the true interaction over a sufficiently wide range of scattering energies will give many-electron eigenvalues very close to the true interaction.

This problem (for electron-electron scattering) is analogous to the problem of electron-ion scattering addressed in the pseudopotential method. In that approach, the aim is to produce a smooth electron-ion potential which reproduces the single-particle eigenvalues of the true system over a range of energies, and has the same single-particle wavefunctions outside some suitably chosen cut-off radius. Such pseudopotentials are generated for the isolated atom but may then be used with a high level of accuracy in molecules and solids

Following the success of norm-conserving pseudopotential methods in the context of the electron-ion scattering problem, we generate from consideration of the two-electron scattering problem a norm-conserving pseudo-interaction which is intended to replace the true $1/r$ electron-electron interaction. This is presented in Section 2 of the paper. Since the electron-electron interaction is repulsive and has no bound states for an isolated pair of electrons, we use, with some minor modifications, the generalized norm-conserving method devised by Hamann [4] to generate pseudopotentials for electron-ion interactions at unbound, scattering state energies. In section 3, discussion of the method for configuration interaction methods is presented. We indicate how standard algorithms for the calculation of two-electron integrals in a Gaussian expansion can be modified for our pseudo-interaction. We have demonstrated the application of the pseudo-interaction to dynamical CI methods whereby configuration state functions are not selected *a priori*, but are included based upon a selection criterion as the calculation proceeds. Hence methods with a predefined number of configurations such as singles and doubles CI, or other excitation truncated methods, are not pertinent to our discussions, but methods such as a Monte-Carlo generation of configurations (MCCI) [5, 6] and the use of a second-order perturbation scheme for the selection of configurations [7] are well-suited to a pseudo-interaction approach. We will find however, that the CI expansions actually introduce very few functions for fitting the cusps for accuracies typically required — hence the belief that the obstacle to convergence in CI calculations is due to fitting the cusps has been found to be *untrue* for calculations

of chemical accuracy.

2 Construction of generalised norm-conserving pseudopotentials for electron-electron interactions

This procedure follows that set out by Hamann [4] for producing generalised norm-conserving pseudopotentials (GNCPP's), with relatively minor modifications. There are two differences between our electron-electron scattering problem and the electron-ion pseudopotential generation treated by Hamann: (i) Only two particles are involved in the generation of the electron-electron pseudo-interaction, so that we do not need to include screening potentials; (ii) because we are solving the scattering problem in the centre of mass frame of the electrons and use the relative coordinate $\mathbf{r}$ of the electrons, the mass of the electron is replaced by the reduced mass for the two-electron system. Using Hartree atomic units throughout, the interaction potential is then $V(r) = 1/r$ and the reduced mass is $1/2$. The absence of screening simplifies some of the steps laid out in Hamann's work. Full technical details of how to generate the pseudo-interaction are given in Ref. [3] and we only briefly discuss some qualitative issues here.

2.1 Two-electron Scattering

The radial Schrödinger equation for the relative motion of two electrons is

$$-\frac{d^2 u_l}{dr^2} + \left(\frac{l(l+1)}{r^2} + (V - \epsilon) \right) u_l = 0, \tag{1}$$

where $u_l(r)$ is r times the wave function in the relative coordinates, with angular momentum l and energy ϵ. In the norm-conserving pseudopotential approach, different scattering potentials are often generated for different values of the angular momentum l. The full many-body wavefunction is anti-symmetric with respect to exchange of any two electrons. Thus, if the spins of the two electrons are parallel, the orbital part of the wave function must have odd parity in their relative separation and the allowed angular momentum l in Eqn. (1) must be odd. The dominant parallel-spin scattering would then have $l = 1$. For singlet (anti-parallel) scattering, the spin part of the two-electron wavefunction is anti-symmetric, so that the orbital part is symmetric and l must be even. In this case the dominant allowed angular momentum is $l = 0$.

Following the usual pseudopotential approach, we might then expect to generate a parallel-spin scattering potential using $l = 1$ and an anti-parallel-spin scattering potential using $l = 0$. In practice, we find that the $l = 0$ potential gives good scattering for both angular momenta and the use of separate parallel- and anti-parallel-spin potentials is unnecessary.

The eigenvalue ϵ is the kinetic energy of the electrons in the centre of mass frame. In the generation of a pseudopotential, the real potential and pseudopotential become identical outside a suitably chosen cut-off radius r_c and are constructed to have identical scattering phase shifts and energy derivative of the phase shift at a reference energy. The choice of ϵ_l is important for large values of the cut-off radius. However, for values of the cut-off radius which one would expect to use in a calculation the choice of ϵ_l is not expected to be crucial.

The choice of an appropriate cut-off radius r_c is determined by the properties of the system in which we plan to use the pseudo-interaction. If r_c is chosen to be extremely small, then the interaction is almost numerically identical to the true interaction. At the other extreme, if the cut-off radius is chosen to be much larger than the system size, the electron-electron interaction will hardly depend at all on the distance between the electrons and we will obtain essentially the properties of a non-interacting system.

In the generation of norm-conserving pseudopotentials for electron-ion interactions, it is generally found that the maximum cut-off radius for accurate transferable pseudopotentials is approximately half the radius at which $u_l(r)$ of the relevant valence state has its outer-most maximum. This forces the pseudo-wave-function to converge to the full-potential wave function somewhat inside this maximum, which typically occurs near the relevant radius for bonding in such states. We found that a similar criterion, applied to the electron pair distribution function, determines the maximum cut-off radius for highly accurate electron-electron pseudo-interactions.

3 CI Convergence and Implementation of The Pseudo-Interactions

3.1 CI Calculations and Pseudointeractions

Although the CI method can give an exact solution of the Schrödinger equation in a finite basis set, it requires an extremely large number of configuration state functions (CSFs), and hence extremely large vector and matrix dimensions. It is generally accepted that the slow convergence of the CI expansion is partly due to the electron-electron cusp, as discussed earlier in this paper. It has been demonstrated, both theoretically and numerically, that the convergence of a CI calculation, using Slater determinants built up from single-particle functions, is proportional to l^{-3}, where l is the maximum angular momentum in the basis set. Explicit inclusion of terms in the inter-electronic distance as in Hylleraas' He work [8], the more modern work of Kutzelnigg and Klopper [9], or the use of explicitly correlated (geminal) Gaussian basis functions [10], can improve the convergence of a CI calculation and the calculation can be found to converge as l^{-6} or better [11]. The accepted reason for the success of methods which explicitly include r_{12} is that they give a correct description of the short-range part of the interaction. Baker *et al* [12] also showed that using basis functions with the same analytic structure as the function one is trying to fit (inclusion of powers of r_{12} and logarithmic terms in r_{12}) can lead to a reduced expansion length, a technique pioneered by Pekeris [13]. However, these methods are outside the mainstream of quantum chemistry, and can not easily avail of the standard numerical tools applied within such calculations, or are only applicable to two electron problems.

An electron-electron interaction potential which is smooth at short-range and finite at the origin will have smooth electron-electron coalescences. Hence it has been generally accepted that pseudo-interactions which are finite at the origin would be expected to give better convergence in terms of the number of expansion functions required to provide a given accuracy in the energy [9, 11, 14, 15, 16], as compared to a pure Coulomb interaction. Although this point had been stated in the literature, there appear to be no numerical expositions of this prior to the numerical study of Prendergast *et al.*[3]. As far as we are aware, this was the first time that the actual convergence of a CI expansion had been examined in the case where the electron-electron

interaction is given by a function which does not contain an electron-electron cusp.

3.2   Evaluation of Two-Electron Gaussian Integrals with Pseudo-Interactions

The implementation of the scattering potential in CI calculations involves fitting the numerically generated pseudo-interaction to a sum of terms which can be evaluated analytically in the Gaussian CI basis functions, as follows:

$$V_{ee} = \text{erf}\frac{(\mu r)}{r} + \sum_{i=1}^{n_G} c_i \exp(-a_i r^2) \qquad (2)$$

Rys quadrature [17] is a standard numerical scheme for the calculation of two-electron Coulomb integrals in a Gaussian basis. The details, such as the calculation of the the number of quadrature roots, their values and weights, as well as the motivation for the Rys quadrature method may be found in the paper by Dupuis, Rys and King [17], and references therein. Details of how to simply modify the Rys quadrature approach to calculate two-electron intergrals for an interaction represented by Eq. (2) are given in Ref. [3]. We have applied the modifications to the calculation of two electron integrals within the ARGOS code, part of the COLUMBUS program package [18].

4   Results and Conclusions

We have applied the pseudo-interaction method to the calculation of correlated atomic energies for helium and beryllium using a sequence of basis functions including up to g functions. As we have described, we have employed the MCCI method for calculation of electronic energies. This is an important feature of our study as the MCCI method is not an excitation truncated method, *i.e.* the number of CSFs to include in a calculation is not *a priori* fixed. Rather, the MCCI method randomly selects CSFs, retains important configurations, and iterates this procedure until the energy (and number of CSFs) converges.

Let us consider what this implies for calculations using the electron-electron pseudo-interaction. When the MCCI method converges, it has a set of CSFs which best represent the total correlation energy for a given CI vector coefficient threshold. Hence the CI vector is the set of "best" CSFs to describe to correlation energy, and based upon exact studies of fitting the correlation cusp using higher angular momentum functions, we would anticipate the CI vector will increase in length as higher angular momentum functions are included into the basis, and that these are included into the calculation primarily by the need to better describe the electron-electron cusps.

We now turn on the pseudo-interaction, and increase the cut-off radius and eliminate the cusps. We would then anticipate that the number of CSFs needed to describe the cusp region is decreased, and that this achieved at little cost to the accuracy in the total energies. Hence, when the MCCI calculation converges with pseudo-interaction replacing the true Coulomb interaction, we would expect to converge to a CI vector with the number of "best" CSFs substantially less than for the full interaction Hamiltonian.

Returning to our numerical studies where we have studied the convergence properties of CI calculations as function of CI vector coefficient threshold, pseudo-interaction cut-off radius, and
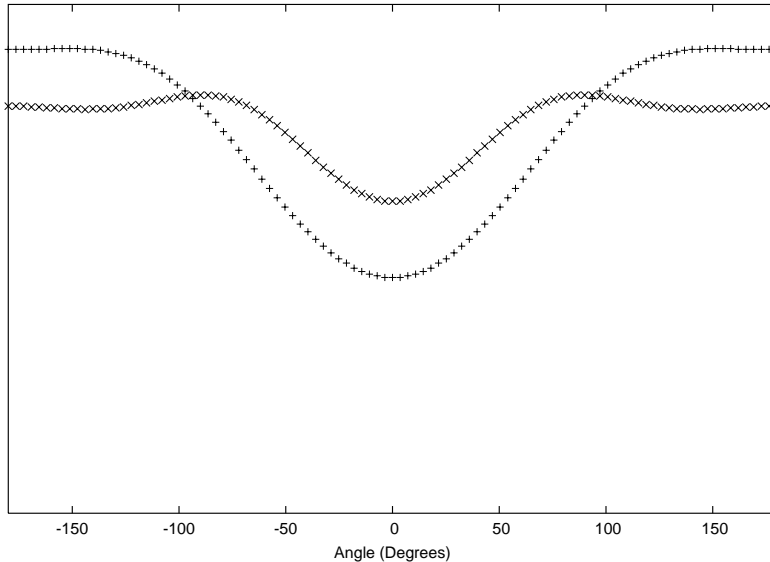
Figure 1: The two-body reduced density matrix calculated for atomic helim calculated using the cc-pvDZ (x) and cc-pvQZ (+) basis sets (vertical axis in arbitray units). The increase in the number of basis functions and in particular the increase in angular momentum in going to the larger basis set improves the description of the cusp region. However, smoothing the cusps does not reduce the effort needed to describe the correlation hole.

angular momentum in the single particle basis expansion [3]. The calculations were performed for He and Be. Without overly belaboring the point, we found that replacement of the pseudo-interaction *did not* significantly reduce the number of CSFs needed to describe the correlated systems (readers seeking the explicit details are referred to ref. [3]). The assumption that the additional CSFs needed in a CI expansion to converge to the full CI (FCI) energy are needed primarily to describe the cusp region is incorrect. This is our primary conclusion.

We now seek to reconcile this result with properties known for treating the cusp. For example, in ref. [19] the asymptotic form of wavefunction as a function of angular momentum is derived for the helium cusp. In the asymptotic regime, higher angular momentum functions ($l > 30$) are required to achieve microHartree accuracy in the total energy. Here we are working to chemical accuracy (milliHartree) and the maximum angular momentum function considered is g ($l = 4$). We have fitted the convergence of the total energy to the asymptotic form and find that, although the general behaviour of the asymptotic form is observed, the coefficients extracted are not equivalent to the asymptotic coefficients. Hence we are not working in the asymptotic region and the requirements to describe the cusp region to chemical accuracy are significantly less demanding. In fig. 1, we plot the the two-body reduced density function $\Gamma(r_1; r_2)$ for atomic helium with one electron fixed at a distance of 0.5 a.u. from the nucleus, and the second electron is allowed to move on a circle of radius of 0.5 a.u. The electron cusp occurs when the two electrons coincide, and as expected, the CI wavefunction improves at the cusp as the basis is increasd. However, even for larger values of angular momentum typically used in CI calculations, the cusp region is not particularly well-described. Smoothing the cusp does not reduce the number of configurations required to describe the vicinity of the electron, and a more accurate representation of the cusp regions does not provide a significant improvement in the

electronic energy.

Finally, we point out that the results of our study are consistent with arguments put forward by Gilbert [20], who in 1963 anticipated the results of our detailed numerical study. Gilbert argued that the cusp region was not the limiting factor for an accurate treatment of the correlation energy, but that intermediate range correlations (i.e. for typical electron-electron separations) are the practical limiting factor to convergence in CI calculations. He argued that the contribution to correlation energy from a poor representation of the cusp is relatively small, and that the use of basis functions relative to a fixed spatial reference were unable to easily treat correlations for typical inter-electron separations. After nearly 40 years, we can now substantiate his considerations.

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