Tools for analysing configuration interaction wavefunctions

Delaney, P., & Greer, J. C. (2003). Tools for analysing configuration interaction wavefunctions. *Computational Materials Science*, 28(2), 240-249. [https://doi.org/10.1016/S0927-0256\(03\)00110-1](https://doi.org/10.1016/S0927-0256(03)00110-1)

Published in:
Computational Materials Science

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Tools for analysing configuration interaction wavefunctions

P. Delaney, J.C. Greer *

NMRC, Prospect Row, Cork, Ireland

Abstract

The configuration interaction (CI) approach to quantum chemical calculations is a well-established means of calculating accurately the solution to the Schrödinger equation for many-electron systems. It represents the many-body electron wavefunction as a sum of spin-projected Slater determinants of orthogonal one-body spin-orbitals. The CI wavefunction becomes the exact solution of the Schrödinger equation as the length of the expansion becomes infinite, however, it is a difficult quantity to visualise and analyse for many-electron problems. We describe a method for efficiently calculating the spin-averaged one- and two-body reduced density matrices $\rho_{\Psi}(\mathbf{r}; \mathbf{r})$ and $\Gamma_{\Psi}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$ of an arbitrary CI wavefunction Ψ . These low-dimensional functions are helpful tools for analysing many-body wavefunctions; we illustrate this for the case of the electron–electron cusp. From ρ and Γ one can calculate the matrix elements of any one- or two-body spin-free operator $\hat{O}$. For example, if $\hat{O}$ is an applied electric field, this field can be included into the CI Hamiltonian and polarisation or gating effects may be studied for finite electron systems.

© 2003 Elsevier B.V. All rights reserved.

PACS: 31.25.Eb; 31.25.Jf; 31.15.Pf; 02.70.Lq

1. Introduction

The configuration interaction (CI) approach to quantum chemical calculations is a method for accurately calculating the solutions to the time-independent Schrödinger equation for a many-electron system such as a molecule,

$$\hat{H}\Psi_n = E_n\Psi_n \quad (1)$$

where n stands for some set of quantum numbers that characterise the eigenstates of $\hat{H}$. In this equation, if the molecule has N electrons then Ψ is a N -body wavefunction $\Psi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_N s_N)$ and the

Hamiltonian operator $\hat{H}$ is the sum of kinetic and Coulomb potential energy contributions

$$\hat{H} = - \sum_{i=1,N} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{i=1,N} U(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2)$$

Here, $U(\mathbf{r})$ is the attractive potential energy of an electron in the Coulomb field of the A atomic nuclei located at positions $\mathbf{R}_a$, $a = 1, \dots, A$,

$$U(\mathbf{r}) = \sum_{a=1,A} \frac{-Z_a e^2}{|\mathbf{r} - \mathbf{R}_a|} \quad (3)$$

The first two terms in Eq. (2) are *one-body* terms, while the final electron–electron Coulomb sum is a *two-body* term. Here, boldface is used to denote three-dimensional vectors.

* Corresponding author. Tel.: +353-21-4904345; fax: +353-21-270271.

E-mail address: jgreer@nmrc.ucc.ie (J.C. Greer).

With CI, we can in principle calculate the electronic eigenstates and eigenenergies of any molecule or atom to an arbitrary precision. The CI approach involves choosing a particular approximate form for the solutions Ψ_n of (1): Ψ_n is approximated as a sum of a finite number of Slater determinants. We then solve this reduced problem using standard iterative matrix diagonalisation techniques and arrive at approximate eigenvalues and eigenvectors: as the number of Slater determinants is increased, $\Psi_n^{\text{CI}} \rightarrow \Psi_n^{\text{exact}}$, for both ground and excited states. However, although configuration interaction wavefunctions can be very accurate, they are very hard to visualise: for N electrons Ψ is a function of $3N$ variables, typically giving 60–600 coordinates. Now visualisation is important for obtaining understanding and in the construction of accurate approximations, and in CI at present this is lacking. So, in this article we describe a method for efficiently analysing and visualising configuration interaction many-electron wavefunctions, by calculating the spin-averaged one- and two-body reduced density matrices $\rho_\Psi(\bar{\mathbf{r}}; \bar{\mathbf{r}}')$ and $\Gamma_\Psi(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1, \bar{\mathbf{r}}'_2)$ of an arbitrary CI wavefunction Ψ . These are low-dimensional functions and are useful in visualising the distribution of the electrons in many-body wavefunctions.

A word about notation: through much of this article we are concerned with calculating $\rho_\Psi(\bar{\mathbf{r}}; \bar{\mathbf{r}}')$ and $\Gamma_\Psi(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1, \bar{\mathbf{r}}'_2)$ with some particular fixed values of $\bar{\mathbf{r}}$ and $\bar{\mathbf{r}}'$ or of $\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, \bar{\mathbf{r}}'_1$ and $\bar{\mathbf{r}}'_2$ in mind. In the process we will encounter expressions involving electron wavefunctions $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ which depend on N vectors $\mathbf{r}_1, \dots, \mathbf{r}_N$. Unbarred vectors are variables: they have no specific value and we will frequently integrate over them (17) or use them for defining wavefunctions (6) or the action of operators (7). The reason for the semicolon and primes in the parameter list is to distinguish row- and column-like quantities. For example, Eq. (17) is a continuous version of a dot-product: Ψ^* is the row vector, and Ψ the column. The primed parameters connect with row indices, the unprimed parameters with column indices and so we use the semicolon to separate these two types of parameters.

The structure of this paper is as follows. In Section 2 we describe the form of the wavefunction

Ψ in CI. In Section 3, we define the first and second order reduced density matrices, and show how the expectation value of any one- or two-body spin-free operator $\hat{O}$ may be calculated from them. In Section 4, we describe how to modify existing CI codes so that they can calculate these quantities efficiently, and in Section 5 we show an example of how knowledge of Γ enables one to visualise the electron–electron cusp in the wavefunction.

2. The configuration interaction expansion of the wavefunction

As we will be calculating $\rho_\Psi(\bar{\mathbf{r}}; \bar{\mathbf{r}}')$ and $\Gamma_\Psi(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1, \bar{\mathbf{r}}'_2)$ from a CI wavefunction Ψ , we will first describe in more detail the form of the wavefunction in CI, and the accuracy of the resulting approximation. The CI expansion represents the total electronic wavefunction as a finite linear expansion

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2 + \dots + c_L \Psi_L \quad (4)$$

of many-body basis states Ψ_μ , with adjustable coefficients c_μ . This set of basis functions spans a subspace S_{CI} , the CI space, and once they are chosen the CI approach then simply varies the coefficients c_μ until we minimise the energy $\langle \Psi, \hat{H} \Psi \rangle$, while preserving normalisation $\langle \Psi, \Psi \rangle = 1$. This leads to a standard *generalised eigenvalue problem*: “generalised” because the many-body basis vectors Ψ_μ are usually not orthogonal.

These basis vectors are named *configuration state functions* (CSFs) or, more descriptively, *spin-projected Slater determinants*, and are of the form

$$\Psi_\mu = \hat{O}_s \hat{A} [\psi_{i(\mu,1)}(\mathbf{r}_1 s_1) \psi_{i(\mu,2)}(\mathbf{r}_2 s_2) \dots \psi_{i(\mu,N)}(\mathbf{r}_N s_N)] \quad (5)$$

$$= \frac{1}{N!} \hat{O}_s \begin{vmatrix} \psi_{i(\mu,1)}(\mathbf{r}_1 s_1) & \dots & \psi_{i(\mu,1)}(\mathbf{r}_N s_N) \\ \dots & \dots & \dots \\ \psi_{i(\mu,N)}(\mathbf{r}_1 s_1) & \dots & \psi_{i(\mu,N)}(\mathbf{r}_N s_N) \end{vmatrix} \quad (6)$$

where $|M|$ is the determinant of the matrix M . We will go through this definition piece by piece. First, $\hat{A}$ is the antisymmetrisation operator [1], a hermitian operator defined by

$$\begin{aligned} \hat{\mathbf{A}}[\psi_1(\mathbf{r}_1 s_1) \cdots \psi_N(\mathbf{r}_N s_N)] \\ = \frac{1}{N!} \sum_P \epsilon_P \psi_1(\mathbf{r}_{P(1)} s_{P(1)}) \cdots \psi_N(\mathbf{r}_{P(N)} s_{P(N)}) \end{aligned} \quad (7)$$

where the sum is over all permutations $P \in S_N$, the group of all permutations of order N , and ϵ_P is the sign of the permutation P . The factor $\frac{1}{N!}$ is chosen in the definition of $\hat{\mathbf{A}}$ because we then have idempotency: $\hat{\mathbf{A}}^2 = \hat{\mathbf{A}}$, i.e. $\hat{\mathbf{A}}$ is a projection operator projecting the general product wavefunction $\psi_1(\mathbf{r}_1 s_1) \cdots \psi_N(\mathbf{r}_N s_N)$ onto the space of antisymmetric wavefunctions. The sum-over-all-permutations together with the ϵ_P factor above is the same pattern as occurs in the definition of the determinant of a matrix [2], which is why we can rewrite Eq. (5) as Eq. (6): hence the term *Slater determinant*.

Second, the one-electron spin orbitals $\psi_i(\mathbf{r}, s)$ are usually chosen from some given finite set: in our code `mccif` [3,4], we first choose an appropriate finite set of spatial molecular orbitals $\phi_i(\mathbf{r})$, $i = 1, \dots, N_{\text{mo}}$, which then spans a subspace of the infinite-dimensional one-electron Hilbert space $L^2(\mathbf{R}^3)$. These could come from a Hartree–Fock or density functional theory calculation. Generally these orbitals are required to be orthonormal, for simplicity of the resulting algebra. A spinor α or β is appended to each molecular orbital resulting in $2N_{\text{mo}}$ spin-orbitals, ψ_i . By selecting any N of these spin-orbitals, we can form a valid N -electron wavefunction by constructing the $N \times N$ Slater determinant from these orbitals, and the different CSFs in the CI expansion (4) correspond to different choices of these ψ_i ; these particular choices are stored in the indexing function $i(\mu, n)$. If there are N electrons and $2N_{\text{mo}}$ possible spin-orbitals, there are $L_{\text{max}} = \binom{N_{\text{mo}}}{N/2} \times \binom{N_{\text{mo}}}{N/2}$ distinct Slater determinants with (say) an equal number of spin up and spin down orbitals ($m_s = 0$) that can be constructed. The total possible number of adjustable coefficients in (4) gets extremely large with increasing N or N_{mo} .

In typical applications, we can neglect the spin-orbit interactions (or treat them later as a perturbation), allowing us to take the exact many-body wavefunction to be in an eigenstate of $\hat{\mathbf{S}}^2$ and $\hat{\mathbf{S}}_z$, with quantum numbers s and m_s respectively. Although a Slater determinant of spin-orbitals will

always be an eigenstate of $\hat{\mathbf{S}}_z$, it will generally not be a pure eigenstate of $\hat{\mathbf{S}}^2$, but will mix in several values of s . This is referred to as *spin contamination*. To solve this, we apply to the wavefunction $\hat{\mathbf{O}}_s$, the *spin-projection operator* [5]. If one thinks of the Slater determinant as resolved along the different eigenspaces of $\hat{\mathbf{S}}^2$ corresponding to $\hat{\mathbf{S}}^2$ values of $\hbar^2 s(s+1)$, where $s = N/2, (N/2) - 1, \dots, 0$ or $1/2$ (depending on whether N is even or odd), then the spin-projection operator $\hat{\mathbf{O}}_s$ simply leaves unchanged the component along the desired s eigenspace and removes all other components. It can be explicitly defined as

$$\hat{\mathbf{O}}_s = \prod_{k \neq s} \frac{\hat{\mathbf{S}}^2 - \hbar^2 k(k+1)}{\hbar^2 s(s+1) - \hbar^2 k(k+1)} \quad (8)$$

where the sum runs over all $k = N/2, (N/2) - 1, \dots, 0$ or $1/2$ except for $k = s$. This operator is hermitian and also electron-symmetric ($[\hat{\mathbf{O}}_s, P] = 0, \forall P \in S_N$). Generally, after spin projection, a CSF can no longer be written as a single Slater determinant, but may be represented as a weighted or *spin-coupled* sum of Slater determinants.

If there are no magnetic fields present, the different m_s levels for this value of s are strictly degenerate, and if one is looking for CI eigenvalues one can pick any value of m_s from the allowed range $-s, -s+1, \dots, s-1, s$. Usually, to simplify algebra involving the spin-projection operators, the *principal case* $m_s = s$ is chosen, and one then builds CSFs belonging to this value of m_s by including $\frac{1}{2}N + m_s$ up electrons and $\frac{1}{2}N - m_s$ down electrons in each determinant. Requiring the CSFs to be eigenstates of $\hat{\mathbf{S}}^2$ and $\hat{\mathbf{S}}_z$ restricts their form and so reduces the maximum length of the CI expansion, however there is still a combinatorially large number of linearly independent CSFs. A satisfying feature of the CI ansatz for the wavefunction is that if the set of one-electron wavefunctions $\phi_i(\mathbf{r})$ is complete for the space $L^2(\mathbf{R}^3)$, and all possible CSFs are included in the CI wavefunction, then the CI expansion (4) is complete [6]. Thus, by increasing the size of the one-body basis set (N_{mo}) and/or the number of terms in the CI expansion (L), we can predict many-body eigenvectors and eigenvalues to arbitrary accuracy.

Further reductions in the length of the expansion to be considered can be obtained by using

other symmetries besides rotations in spin-space. If the molecule has a non-trivial spatial symmetry group G , the many-electron eigenstates Ψ_n must transform according to one or another of the irreducible representations of G , further restricting the structure of the CSFs and so decreasing the dimension of the CI space.

Once the form of the wavefunction has been decided, the molecular system to be studied is specified by defining the Hamiltonian operator: if the atomic numbers and positions are given, the Hamiltonian (2) is known. To calculate the approximate eigenvalues in the CI space, one first calculates the matrix

$$H_{\mu\nu} = \langle \Psi_\mu, \hat{H} \Psi_\nu \rangle, \quad 1 \leq \mu, \nu \leq L \quad (9)$$

using the Slater–Condon–Harris (SCH) rules [1] for calculating matrix elements between spin-projected determinants, and then solves the generalised eigenvalue problem

$$H_{\mu\nu} C_\nu = E S_{\mu\nu} C_\nu \quad (10)$$

where $S_{\mu\nu}$ is the overlap matrix of the basis Ψ_μ , $S_{\mu\nu} = \langle \Psi_\mu, \Psi_\nu \rangle$. As can be seen from (10), the different configuration state functions Ψ_μ are coupled by the non-zero matrix elements of $\hat{H}$ and $\hat{S}$ and interact with each other: this is the origin of the name *configuration interaction*.

It is well known that of the very large number of possible linearly independent CSFs only a small number contribute to an improvement in the energy and/or the wavefunction. To make the eigenvalue problem computationally feasible, we wish to obtain shorter CI expansions while preserving the accuracy of the method: there are various ways of doing this which we need not go into. Our procedure for calculating the density matrices will work for any CI wavefunction Ψ generated from a set of spin-projected determinants, and indeed, any CI expansion may be represented in this form.

3. Reduced density matrices

Given any N -electron CI wavefunction Ψ of the form (4), we first define the density matrix corresponding to Ψ as the operator $|\Psi\rangle\langle\Psi|$. Density

matrices are more general than wavefunctions, for example, if a part a of a quantum mechanical system $a+b$ is to be studied, then generally there will be no wavefunction Ψ_a from which all subsystem properties can be deduced as expectation values. However, there is such a density matrix D_a . For a clear discussion of density matrices, see [7].

To define the density matrix of a subsystem, we must be able to identify the Hilbert space $\mathcal{E}_H$ for the total system $a+b$ as the tensor product of two separate Hilbert spaces $\mathcal{E}_H^a$ and $\mathcal{E}_H^b$, with bases $|k_a\rangle$ and $|l_b\rangle$. We take it that we know the wavefunction of the total system Ψ , and we define the system density matrix as $\hat{D} = |\Psi\rangle\langle\Psi|$. We define the density matrix $\hat{D}_a$ of the subsystem a by tracing over the basis of $\mathcal{E}_H^b$

$$\hat{D}_a = \text{Tr}_b \hat{D}, \quad \langle k_a, \hat{D}_a k'_a \rangle = \sum_{l_b} \langle k_a l_b, \hat{D} k'_a l_b \rangle \quad (11)$$

Now observables of the form $\hat{A}_a \otimes \hat{I}_b$ describe measurements relating to the subsystem a , and their expectation values $\text{Tr} \hat{D} (\hat{A}_a \otimes \hat{I}_b)$ can be computed knowing only the matrix $\hat{D}_a$:

$$\langle \hat{A}_a \rangle_\Psi = \text{Tr} \hat{D} (\hat{A}_a \otimes \hat{I}_b) \quad (12)$$

$$= \sum_{k_a, k'_a, l_b, l'_b} \langle k_a l_b, \hat{D} k'_a l'_b \rangle \langle k'_a l'_b, \hat{A}_a \otimes \hat{I}_b k_a l_b \rangle \quad (13)$$

$$= \sum_{k_a, k'_a, l_b} \langle k_a l_b, \hat{D} k'_a l_b \rangle \langle k'_a, \hat{A}_a k_a \rangle \quad (14)$$

$$= \text{Tr} \hat{D}_a \hat{A}_a \quad (15)$$

Our Hilbert space $\mathcal{E}_N$ for the N -electron problem is the (antisymmetric) tensor product $\otimes_{i=1,N}^A \mathcal{E}_1$ of N identical copies of the Hilbert space of one electron $\mathcal{E}_1 = L^2(\mathbf{R}^3) \otimes \{1, -1\}$. The factor of N is what makes the CI wavefunction hard to visualise. However, as one can see from the Hamiltonian (2), all of the terms that influence electron motion are either one-body (refer to one electron's coordinates at a time, like the kinetic energy and the nuclear Coulomb field) or are two-body (referring to pairs of electron coordinates at a time, such as the electron–electron repulsion $\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$). Furthermore, all of the observables we commonly wish to evaluate are either one- or two-body operators. It would seem that for our purposes many of the degrees of

freedom in Ψ are irrelevant, and so we can follow the above procedure and trace over $N - 1$ of the one-particle spaces to obtain the one-body reduced density matrix $\rho_\Psi(\bar{\mathbf{r}}s; \bar{\mathbf{r}}'s')$ defined on $\mathcal{E}_1$ or over $N - 2$ of the spaces to obtain $\Gamma_\Psi(\bar{\mathbf{r}}_1s_1, \bar{\mathbf{r}}_2s_2; \bar{\mathbf{r}}'_1s'_1, \bar{\mathbf{r}}'_2s'_2)$, defined on $\mathcal{E}_1 \otimes^A \mathcal{E}_1$. To simplify matters further, in this paper we consider the *spin-averaged* reduced density matrices, where we additionally trace over the remaining spin degrees of freedom. Thus, we define the spin-averaged one-body reduced density matrix $\rho_\Psi(\bar{\mathbf{r}}; \bar{\mathbf{r}}')$ corresponding to a wavefunction Ψ by

$$\rho_\Psi(\bar{\mathbf{r}}; \bar{\mathbf{r}}') = N \sum_{s_1 \dots s_N} \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Psi^*(\bar{\mathbf{r}}'s_1, \mathbf{r}_2s_2, \dots, \mathbf{r}_Ns_N) \times \Psi(\bar{\mathbf{r}}s_1, \mathbf{r}_2s_2, \dots, \mathbf{r}_Ns_N) \quad (16)$$

The inclusion of the factor N in the definition of ρ insures that if the wavefunction is normalised ($\langle \Psi, \Psi \rangle = 1$), then the diagonal density matrix $\rho_\Psi(\bar{\mathbf{r}}; \bar{\mathbf{r}})$ is the electronic number density at the point $\bar{\mathbf{r}}$: the integrals $\int d\mathbf{r}_2 \dots d\mathbf{r}_N$ are a continuous version of a matrix trace.

Similarly, we define the spin-averaged two-body reduced density matrix $\Gamma_\Psi(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1, \bar{\mathbf{r}}'_2)$ by

$$\Gamma_\Psi(\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2) = N(N-1) \sum_{s_1 \dots s_N} \int d\mathbf{r}_3 \dots d\mathbf{r}_N \Psi^*(\bar{\mathbf{r}}'_1s_1, \bar{\mathbf{r}}'_2s_2, \mathbf{r}_3s_3, \dots, \mathbf{r}_Ns_N) \times \Psi(\bar{\mathbf{r}}_1s_1, \bar{\mathbf{r}}_2s_2, \mathbf{r}_3s_3, \dots, \mathbf{r}_Ns_N) \quad (17)$$

With this factor of $N(N-1)$, we find that $\Gamma_\Psi(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2) \equiv \Gamma_\Psi(\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}_1\bar{\mathbf{r}}_2)$ gives us the probability density for observing an electron pair occupying the positions $\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2$. For example, $\Gamma_\Psi(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2)$ is useful for observing the tendency of electrons to avoid each other, due to their mutual Coulomb repulsion; we demonstrate this in Section 5. As stated above, we can calculate the expectation value of the Hamiltonian (2) knowing $\hat{\rho}_\Psi$ and $\hat{\Gamma}_\Psi$:

$$\langle \Psi, \hat{H} \Psi \rangle = \text{Tr} \hat{\rho}_\Psi \left(-\frac{\hbar^2}{2m} \nabla^2 + U(\bar{\mathbf{r}}) \right) + \frac{1}{2} \text{Tr} \hat{\Gamma}_\Psi \frac{e^2}{|\bar{\mathbf{r}}_1 - \bar{\mathbf{r}}_2|} \quad (18)$$

Higher order reduced density matrices can also be defined; the highest order is N at which level we

recover the full density matrix $D = |\Psi\rangle\langle\Psi|$. The usefulness of the one- and two-body reduced density matrices is that they contain all the information necessary to calculate the energy $\langle \Psi, \hat{H} \Psi \rangle$ exactly while involving much fewer degrees of freedom (due to their low dimensionality) than the full wavefunction Ψ . Thus, they are easier to visualise and manipulate computationally. For example, instead of varying the many-body wavefunction Ψ , it is also possible to vary the one-body or one- and two-body reduced density matrices until one finds the lowest energy state possible, giving the ground state of the system in question [8]. The advantage of this approach is that these are conceptually simpler quantities and because of their low dimensionality should require less computer memory to store, for example if stored on a grid.

4. Computation of the reduced density matrices

Having described the CI form of the wavefunction (4) and defined the one- and two-body reduced density matrices ρ and Γ (16) and (17), we now describe the operation of our programs for calculating the ρ and Γ of a given CI wavefunction Ψ , `mccilbodydens.f` and `mccil2bodydens.f`, respectively. We wish to calculate the integrals (16) and (17) for some given values of $\bar{\mathbf{r}}; \bar{\mathbf{r}}'$ or $\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2$. Our strategy is to write each integral as the expectation value of a particular operator, $\hat{\rho}_{\bar{\mathbf{r}}; \bar{\mathbf{r}}}'$ for the one-body density matrix ρ and $\hat{\Gamma}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}$ for the two-body density matrix Γ . The purpose of expressing the desired numbers $\rho(\bar{\mathbf{r}}; \bar{\mathbf{r}}')$ and $\Gamma(\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2)$ as expectation values of operators is that there are well-known rules, the SCH rules [1], for calculating the expectation value of operators in a given CI wavefunction Ψ . These rules are coded in the CI program `mccil.f` [3,4] to evaluate the matrix elements $H_{\mu\nu}$ (9), so if we can mathematically express each integral (16) and (17) as the expectation value of an operator, the extra amount of coding needed to calculate these integrals will be minimal: essentially two new functions `rho(i, j, r, r')` and `gamma(i, j, k, l, r1, r2, r1', r2')` must be written, and then inserted in the SCH routine instead of the existing kinetic and nuclear

one-electron integrals (for ρ) and the two-electron Coulomb potential integrals (for Γ).

We will now construct operators $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^\rho$ and $\hat{\beta}_{\mathbf{r}_1\mathbf{r}_2;\mathbf{r}'_1\mathbf{r}'_2}^\Gamma$ which give the required numbers as expectation values:

$$\rho_\Psi(\mathbf{r};\mathbf{r}') = \langle \Psi, \hat{\beta}_{\mathbf{r}\mathbf{r}'}^\rho \Psi \rangle \quad (19)$$

$$\Gamma_\Psi(\mathbf{r}_1\mathbf{r}_2;\mathbf{r}'_1\mathbf{r}'_2) = \langle \Psi, \hat{\beta}_{\mathbf{r}_1\mathbf{r}_2;\mathbf{r}'_1\mathbf{r}'_2}^\Gamma \Psi \rangle \quad (20)$$

These operators depend on the given vectors $\mathbf{r}, \mathbf{r}'$ and $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2$, respectively, but are as usual independent of the wavefunction whose density matrices we are calculating. Now for the SCH rules to be applicable, the operators $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^\rho$ and $\hat{\beta}_{\mathbf{r}_1\mathbf{r}_2;\mathbf{r}'_1\mathbf{r}'_2}^\Gamma$ must be spin-free, electron-symmetric and at most two-body in complexity. This requirement of electron-symmetry will give us a little trouble.

Consider first the first order reduced density matrix ρ . After looking at Eq. (16), we see that we can write the integral giving the value of $\rho_\Psi(\mathbf{r};\mathbf{r}')$ as the expectation value of the operator $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^{\rho(1)} = N\hat{b}_{\mathbf{r}\mathbf{r}'}^{\rho(1)}$

$$\rho_\Psi(\mathbf{r};\mathbf{r}') = \langle \Psi, N\hat{b}_{\mathbf{r}\mathbf{r}'}^{\rho(1)} \Psi \rangle \quad (21)$$

where $\hat{b}_{\mathbf{r}\mathbf{r}'}^{\rho(1)}$ is defined by its action on wavefunctions $[\hat{b}_{\mathbf{r}\mathbf{r}'}^{\rho(1)} \Psi](\mathbf{r}_1s_1, \dots, \mathbf{r}_Ns_N) = \delta(\mathbf{r}_1 - \mathbf{r}') \Psi(\mathbf{r}_1s_1, \dots, \mathbf{r}_Ns_N)$ (22)

This operator is a one-body operator which, by inspection, is spin-free. It is non-hermitian: as it is required to be if its expectation value is to give us $\rho_\Psi(\mathbf{r};\mathbf{r}')$, which is in general a complex quantity. However, it is not symmetric in the electron coordinates: more formally, it does not commute with every permutation $P \in S_N$. (One can see by inspection that it singles out the first coordinate $\mathbf{r}_1$.) Although it does yield the correct expectation value, for the SCH rules to apply we need to be able to permute the antisymmetrisation operator $\hat{A}$ past $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^{\rho(1)}$, and this we can not do. To explain why electron symmetry is important, we reproduce Eq. (1) in Harris's paper [1]; we consider the matrix element of the many-body operator $\hat{\beta}$ between two CSFs

$$\langle \Psi_\mu | \hat{\beta} | \Psi_\nu \rangle = \langle \hat{A} \hat{O}_s \Xi_\mu \Theta_\mu | \hat{\beta} | \hat{A} \hat{O}_s \Xi_\nu \Theta_\nu \rangle \quad (23)$$

$$= \langle \Xi_\mu \Theta_\mu | \hat{O}_s \hat{\beta} \hat{A} | \Xi_\nu \Theta_\nu \rangle \quad (24)$$

where $\Psi_\nu = \hat{A} \hat{O}_s \Xi_\nu \Theta_\nu$ is one configuration, with Ξ_ν being a simple product of orthonormal spatial orbitals (e.g. $\Xi_\nu = \phi_1(\mathbf{r}_1)\phi_3(\mathbf{r}_2) \cdots \phi_{12}(\mathbf{r}_N)$) and Θ_ν is a simple product of spin functions, (e.g. $\Theta_\nu = \alpha(s_1)\beta(s_2) \cdots \alpha(s_N)$), and similarly for Ψ_μ . In going from the first line (23) to the second line (24) we can see the importance of being able to commute $\hat{A}$ past $\hat{\beta}$; after this is done, one can use the projection property $\hat{A}^2 = \hat{A}$ to reduce the double sum over $P, P' \in S_N$ in the first line to a single sum over $P \in S_N$ in the second. We also note that we have used the spin-free property to commute $\hat{O}_s$ past $\hat{\beta}$. All of the subsequent manipulations in Harris's paper depend on this simplification, so we see that electron symmetry is an essential property of the operator $\hat{\beta}$ if we wish to apply the SCH rules to it; thus our first guess $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^{\rho(1)}$ will not do.

What is needed to obtain the desired operator is to symmetrise $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^{\rho(1)}$ over all coordinates, and then correct the scale of the operator by dropping the prefactor of N . Thus, we see that we can write the integral giving the value of $\rho_\Psi(\mathbf{r};\mathbf{r}')$ as the expectation value of the operator $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^\rho$

$$\rho_\Psi(\mathbf{r};\mathbf{r}') = \langle \Psi, \hat{\beta}_{\mathbf{r}\mathbf{r}'}^\rho \Psi \rangle \quad (25)$$

where $\hat{\beta}_{\mathbf{r}\mathbf{r}'}^\rho = \sum_{i=1}^N \hat{b}_{\mathbf{r}\mathbf{r}'}^{\rho(i)}$ is a sum of identical one-electron operators, each acting on the coordinate number i , and is defined by its action on wavefunctions

$$[\hat{\beta}_{\mathbf{r}\mathbf{r}'}^\rho \Psi](\mathbf{r}_1s_1, \dots, \mathbf{r}_Ns_N) = \sum_{i=1, N} [\hat{b}_{\mathbf{r}\mathbf{r}'}^{\rho(i)} \Psi](\mathbf{r}_1s_1, \dots, \mathbf{r}_Ns_N) \quad (26)$$

$$= \sum_{i=1, N} \delta(\mathbf{r}_i - \mathbf{r}') \Psi(\mathbf{r}_1s_1, \dots, \mathbf{r}_i s_i, \dots, \mathbf{r}_Ns_N) \quad (27)$$

This operator is again a non-hermitian one-body operator which is spin-free and, this time, symmetric in the electron coordinates. Hence, we can apply the SCH rules to calculate its matrix elements between CSFs and thus its expectation value in the given CI state Ψ , giving us $\rho_\Psi(\mathbf{r};\mathbf{r}')$. These rules are useful because they reduce the $3N - 3$ -dimensional integral (16) to a sum of 3-dimensional *one-electron integrals* of the form

$$\langle \phi_i, \hat{b}_{\mathbf{r}\mathbf{r}'}^\rho \phi_j \rangle = \int d\mathbf{r} d\mathbf{r}' \phi_i^*(\mathbf{r}) \hat{b}_{\mathbf{r}\mathbf{r}'}^\rho(\mathbf{r}, \mathbf{r}') \phi_j(\mathbf{r}') \quad (28)$$

$$= \phi_i^*(\mathbf{r}') \phi_j(\mathbf{r}) \quad (29)$$

where the integral $\int d\mathbf{r}d\mathbf{r}'$ is a continuous version of the matrix quadratic form $u_k M_{kl} v_l$. The reduction here of N -electron expectation values to integrals involving only one electron coordinate $\mathbf{r}$ at a time is the origin of the name *one-body terms*. In our case, because of the special form of $\hat{b}_{\mathbf{r},\mathbf{r}'}^\rho$ the 3-dimensional integrals above have simplified even further. In the SCH rules, these integrals are then weighted by Sanibel coefficients, which capture the action of the spin-projection operator $\hat{O}_s$: explicit formulae are given in [1].

Similarly for the two-body reduced density matrix $\Gamma_\Psi(\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2)$. From the structure of Eq. (17) we might start by defining $\hat{a}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij}$ by its action on wavefunctions according to the formula

$$\begin{aligned} & \hat{a}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij} \Psi(\mathbf{r}_1 s_1, \dots, \mathbf{r}_N s_N) \\ &= \delta(\mathbf{r}_i - \bar{\mathbf{r}}'_1) \delta(\mathbf{r}_j - \bar{\mathbf{r}}'_2) \\ & \quad \times \Psi(\mathbf{r}_1 s_1, \dots, \bar{\mathbf{r}}_1 s_i, \dots, \bar{\mathbf{r}}_2 s_j, \dots, \mathbf{r}_N s_N) \end{aligned}$$

We indeed find that $\langle \Psi, N(N-1) \hat{a}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma 12} \Psi \rangle = \Gamma_\Psi(\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2)$ as we require. However, this operator is not electron-symmetric: it clearly singles out coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. Again, we can solve this by symmetrising, defining

$$\hat{\beta}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^\Gamma = \sum_{i \neq j} \hat{a}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij} \quad (30)$$

which gives us the same expectation value (again because of the antisymmetry of the wavefunction) and is electron-symmetric. This $\hat{\beta}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^\Gamma$ is the correct many-body operator, but examination of the SCH rules reveal a further requirement, not present for one-body operators: we must write $\hat{\beta}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^\Gamma$ in the form $\hat{\beta}^\Gamma = \sum_{i < j} \hat{b}^{\Gamma ij}$, where each $\hat{b}^{\Gamma ij}$ acts only on coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$, and where the sum is now only over $\frac{N(N-1)}{2}$ coordinate pairs. The Coulomb formula $\sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$ is an example of such a decomposition, and this operator $\hat{b}^{\Gamma ij}$ is needed as it will appear later in the SCH formulae [1,4], just as $\hat{b}^{\rho i}$ did for ρ .

To do this, we just pair up terms (i, j) and (j, i) in the definition above (30), that is, we define $\hat{b}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij} = \hat{a}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij} + \hat{a}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ji}$ and then find

$$\hat{\beta}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^\Gamma = \sum_{i < j} \hat{b}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij} \quad (31)$$

We note that as $\hat{\beta}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^\Gamma$ is totally electron-symmetric, and as we sum only over $\frac{N(N-1)}{2}$ pairs, $\hat{b}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij}$ itself must have some symmetry: it is symmetric in the coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$. This property is used in the derivation of the SCH rules, and this is what was missing from $\hat{a}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma ij}$. Thus, we can apply the SCH rules for two-body terms, and find that the N -electron expectation value $\langle \Psi, \hat{\beta}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^\Gamma \Psi \rangle$ can be expressed as a sum of *two-electron integrals* of the form

$$\begin{aligned} \langle \phi_i \phi_j, \hat{b}_{\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2}^{\Gamma 12} \phi_k \phi_l \rangle &= \phi_i^*(\bar{\mathbf{r}}'_1) \phi_j^*(\bar{\mathbf{r}}'_2) \phi_k(\bar{\mathbf{r}}_1) \phi_l(\bar{\mathbf{r}}_2) \\ &+ \phi_i^*(\bar{\mathbf{r}}'_2) \phi_j^*(\bar{\mathbf{r}}'_1) \phi_k(\bar{\mathbf{r}}_2) \phi_l(\bar{\mathbf{r}}_1) \end{aligned} \quad (32)$$

Again, this reduction of the $6N$ dimensional N -electron expectation value to a sum of 6-dimensional two-electron integrals is the origin of the name *two-body terms* for interactions like the electron–electron Coulomb repulsion.

Now we come to the point of our strategy in expressing the desired integrals (16) and (17) as the expectation values of operators. Our CI code `mccif` already includes subroutines where it calculates the matrix elements of the nuclear potential $\sum_{a=1,A} U(\mathbf{r}_a)$ (3) and of the electron–electron Coulomb interaction $\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$, as these are needed for constructing the matrix $H_{\mu\nu}$ (9). The one-body SCH rules do not depend on the nature of the particular operator we are dealing with; thus, for the nuclear potential, we just supply the values of the one-electron matrix elements $\langle \phi_i, \hat{U} \phi_j \rangle$ at an appropriate place in the code which implements the one-body rules, and similarly for the two-body rules. So, now that we have ρ_Ψ and Γ_Ψ as expectation values of operators, we can adapt our existing CI code easily so that it can calculate these numbers: for the calculation of $\rho_\Psi(\bar{\mathbf{r}}; \bar{\mathbf{r}}')$, all we need do is replace occurrences of the kinetic and nuclear one-electron integrals with calls to a function `rho(i, j, \bar{\mathbf{r}}, \bar{\mathbf{r}}')` which returns the value of the one-electron integral

$$\langle \phi_i, \hat{b}_{\bar{\mathbf{r}}\bar{\mathbf{r}}}^\rho \phi_j \rangle = \phi_i^*(\bar{\mathbf{r}}') \phi_j(\bar{\mathbf{r}}) \quad (33)$$

and for $\Gamma_\Psi(\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1\bar{\mathbf{r}}'_2)$, we just replace occurrences of the electron–electron Coulomb two-body integrals with calls to a function `gamma(i, j, k,`

$l, \bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, \bar{\mathbf{r}}'_1, \bar{\mathbf{r}}'_2$) which yields the value of the two-electron integral

$$\langle \phi_i \phi_j, \hat{b}_{\bar{\mathbf{r}}_1 \bar{\mathbf{r}}_2, \bar{\mathbf{r}}'_1 \bar{\mathbf{r}}'_2}^F \phi_k \phi_l \rangle = \phi_i^*(\bar{\mathbf{r}}'_1) \phi_j^*(\bar{\mathbf{r}}'_2) \phi_k(\bar{\mathbf{r}}_1) \phi_l(\bar{\mathbf{r}}_2) + \phi_i^*(\bar{\mathbf{r}}'_2) \phi_j^*(\bar{\mathbf{r}}'_1) \phi_k(\bar{\mathbf{r}}_2) \phi_l(\bar{\mathbf{r}}_1) \quad (34)$$

These two functions are the only new coding needed, and calculating these functions reduces to the calculation of the value of the molecular orbitals $\phi_i, i = 1, \dots, N_{\text{mo}}$ at the points $\bar{\mathbf{r}}$ and $\bar{\mathbf{r}}'$ (for ρ_ψ) or at $\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2, \bar{\mathbf{r}}'_1$ and $\bar{\mathbf{r}}'_2$ (for Γ_ψ). For these functions to be able to calculate $\phi_i(\mathbf{r})$, it is necessary to pass enough information about the atomic basis sets, atomic positions, and molecular orbital coefficients from the initial Hartree-Fock calculation into our programs. Our codes `mccilbodydens.f` and `mccil2bodydens.f` are versions of our main CI code `mccil.f` [3,4] with extra subroutines added which read in the required extra data from the files **coord**, **basis**, **control** and **mos**, output from the program TURBOMOLE [9]. These files contain all the information required for the determination of the molecular orbitals, and definition of the Hamiltonian (2). The definition of the CI basis vectors is read from the file **civ_out** (appropriately renamed **civ_in**) as generated by the program `mccil.f`. Specification of the spin states and occupancies is provided via the `mccil.f` input file **mccil.in**, again file details and formats may be found in [3,4,9]. The two codes themselves are written in Fortran 77 and comprise 4066 lines of code (for `mccilbodydens.f`) and 5928 lines of code (for `mccil2bodydens.f`). Both programs are modular in form and are extensively commented, so they should be relatively easy to alter. For example, if instead of running with a set of CSF's generated by our CI program `mccil.f`, the user wishes to use another CI program, only a few subroutines must be changed: mostly data input routines that need to be adjusted to the format of user data, such as the subroutine `restart.f` in our codes that reads in the set of CSF's from the file **civ_in**. To give a sense of the structure of the codes, a schematic outline of the program `mccil2bodydens.f` for calculating $\Gamma_\psi(\bar{\mathbf{r}}_1 \bar{\mathbf{r}}_2; \bar{\mathbf{r}}'_1 \bar{\mathbf{r}}'_2)$ is displayed in Fig. 1. To obtain the free programs `mccilbodydens.f` and `mccil2bodydens.f`, send an email to jgreer@nmrc.ucc.ie.

Fig. 1. Schematic outline of the program `mccil2bodydens.f`.

5. Example: the electron–electron cusp

As an example of the power of the reduced density matrices for visualising electronic behaviour, we will examine the cusp in the electronic wavefunction Ψ as two electrons approach each other. Now the divergence of the e^2/r electron–electron Coulomb repulsion produces an infinite potential energy at electron coalescences. As the true many-body wavefunction Ψ is an eigenstate of the Schrödinger equation $\hat{H}\Psi = E\Psi$, the local energy $\hat{H}\Psi/\Psi = E$ at such coalescences does not diverge, being balanced by an equal divergence in the electronic kinetic energy: the true wavefunction has a cusp at $r_{ij} = 0$ (a similar behaviour takes place at an atomic nucleus, for example, in the hydrogen 1s orbital at $r = 0$). Now the CI expansion (4) is a finite sum of smooth functions, thus it is differentiable, and at no finite order do we find a cusp. However, as we increase the quality of our

Fig. 2. The two-body reduced density matrix $\Gamma(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2)$ for atomic helium, calculated using the cc-pvDZ (dotted) and cc-pvQZ (solid) basis sets. Here, $|\bar{\mathbf{r}}_1| = |\bar{\mathbf{r}}_2| = 1$ a.u.

one-electron basis set $\phi_i(\mathbf{r})$, we would expect that we could produce a smooth approximate wavefunction which approaches a cusp behaviour. It is a common assumption in the electronic structure community that describing accurately the electron–electron cusp is essential for attaining “chemical accuracy” (~ 1 milliHartree), and that higher angular momentum basis sets and consequently longer CI expansions are the price one needs to pay for this. However, in a recent study [10,11] the electron–electron interaction was replaced by a pseudo-interaction, just as the electron–nucleus interaction is commonly replaced by a pseudopotential in electronic structure calculations. It was expected that this smoother interaction, which would not generate a cusp, could be accurately described by far fewer CI configurations than the real interaction. However, to chemical accuracy, this was not found to be the case: describing the cusp accurately is not essential if one wants to predict energies at the milliHartree level.

We could have seen this directly from Fig. 2 which graphs $\Gamma(\bar{\mathbf{r}}_1, \bar{\mathbf{r}}_2) \equiv \Gamma(\bar{\mathbf{r}}_1\bar{\mathbf{r}}_2; \bar{\mathbf{r}}_1\bar{\mathbf{r}}_2)$, the probability of an electron being found at $\bar{\mathbf{r}}_1$ if another electron is at $\bar{\mathbf{r}}_2$. Here, the system is atomic helium, and both electrons are at a radius of 1 a.u., with one electron being fixed while we vary the angle between it and the other electron from $-\pi$ to π . We study this function for two CI wavefunctions, one built on a one-electron orbital set ϕ_i constructed from a cc-pvDZ atomic basis set (medium quality), and one built on a different set of molecular orbitals ϕ'_i

which were in turn constructed from a higher quality cc-pvQZ atomic basis set. The higher quality wavefunction Ψ_{QZ} is of chemical accuracy [10], but its description of the cusp is no better: visually, the electron probability density is still quite smooth. Thus from the graph we can see immediately that getting an accurate cusp in the wavefunction is simply not a prerequisite for chemical accuracy.

6. Conclusions

A method and overview of programs for calculating spin averaged one-body and two-body reduced density matrices has been presented. Using our approach, the required code changes to our existing CI program are minimal. We have also given the form of the wavefunction we consider.

From the one-body reduced one-body density matrix, the diagonal components allows for the determination of the electronic charge density from CI wavefunctions. In general, the one-body reduced density matrix allows for the study of quantities which can be defined as acting separately on each electron (e.g. Eq. (3)), while maintaining the full role of the many-body interactions. This capability is required for example in studies of spintronics, quantum computing, and in general, for the study of a single particle models, while exploring the effects of many-body correlations.

The reduced two-body density matrix has been presented, and its role in the treatment of elec-

tronic correlation has been demonstrated for the case of the electron–electron cusp. The reduced two-body density matrix is at the very heart of many-electron theory, as it contains *all* the two-body correlations of a many-body system. A detailed study of the two-body reduced density matrix yields insight into the treatment of electronic correlation, and can contribute to development of accurate approximations to many-body computations, including CI treatments, quantum Monte Carlo methods, and exchange–correlation functionals for density functional theory.

Acknowledgements

This work has been funded by the Irish Research Council for Science, Engineering and Technology (IRCSET) and through the European Union project Nanotcad IST-1999-10828.

References

- [1] F.E. Harris, Open-shell orthogonal molecular orbital theory, *J. Chem. Phys.* 46 (7) (1967) 2769–2776.
- [2] S. Axler, *Linear Algebra Done Right*, Springer-Verlag, 1996.
- [3] J.C. Greer, Monte Carlo configuration interaction, *J. Comp. Phys.* 146 (1998) 181–202.
- [4] L. Tong, M. Nolan, T. Cheng, J.C. Greer, A Monte Carlo configuration generation computer program for the calculation of electronic states of atoms, molecules and quantum dots, *Comp. Phys. Comm.* 131 (2000) 142–163.
- [5] P.-O. Löwdin, Quantum theory of many-particle systems. III. Extension of the Hartree–Fock scheme to include degenerate systems and correlation effects, *Phys. Rev.* 97 (1955) 1509–1520.
- [6] P.-O. Löwdin, Quantum theory of many-particle systems. I. Physical interpretation by means of density matrices, natural spin–orbitals, and convergence problems in the method of configurational interaction, *Phys. Rev.* 97 (1955) 1474–1489.
- [7] R. Balian, *From Microphysics to Macrophysics*, vol. 1, Springer-Verlag, Heidelberg, 1991.
- [8] M. Head-Gordon, Y. Shao, C. Saravanan, C.A. White, Curvy steps for density-matrix based energy minimization: tensor formulation and toy applications, *Mol. Phys.* 101 (2003) 37–43.
- [9] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Electronic structure calculations on workstation computers: the program system Turbomole, *Chem. Phys. Lett.* 162 (1989) 165–169.
- [10] D. Prendergast, M. Nolan, C. Fillipi, S. Fahy, J.C. Greer, Impact of electron–electron cusp on configuration interaction energies, *J. Chem. Phys.* 115 (4) (2001) 1626–1634.
- [11] S. Fahy, P. Delaney, J.C. Greer, Pseudo-interactions and the electron–electron cusp, *Psi-k Scientific Highlight* 54. Available from <<http://psi-k.dl.ac.uk/psi-k/highlights.html>>.