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## Second order coalescence conditions of molecular wave functions

David P. Tew<sup>a)</sup>

Institut für Physikalische Chemie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

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Kato's cusp condition gives the exact first order dependence of molecular wave functions on interparticle separation near the coalescence of two charged particles. We derive conditions correct to second order in interparticle separation, which concern second order derivatives of the wave function at the coalescence point. For identical particle coalescence, we give equations correct to third order. In addition to a universal, particle dependent term, a system and state dependent term arises in the higher order conditions, which we interpret as an effect of Coulombic screening. We apply our analysis to the standard orbital-based methods of quantum chemistry and discuss the implications for Jastrow- and R12-type correlation factors. © 2008 American Institute of Physics. [DOI: 10.1063/1.2945900]

### I. INTRODUCTION

The eigenfunctions of the nonrelativistic electronic Schrödinger equation are continuous throughout configuration space and the first order partial derivatives are bounded, but discontinuous at the Coulomb-type singular points of the potential.<sup>1,2</sup> In his fundamental work proving these statements, Kato also characterized the resulting cusps in molecular wave functions at the derivative discontinuities. In atomic units, Kato's cusp conditions may be stated as

$$\widetilde{\left. \frac{\partial \psi}{\partial r_{12}} \right|}_{r_{12}=0} = \gamma \psi(r_{12}=0), \quad (1)$$

where  $\psi$  is a configurational eigenfunction of the fixed nuclei Schrödinger equation and  $r_{12}$  is the interparticle separation.  $\gamma$  takes the value of minus the nuclear charge,  $Z$ , for electron-nucleus coalescence and  $\frac{1}{2}$  for electron-electron coalescence. The tilde indicates an average over a sphere around the singularity. The importance of Kato's cusp conditions for trial wave functions is well known, for example, when computing properties such as cross sections for double ionization of atoms by electron or photon impact,<sup>3</sup> or positron-molecule scattering,<sup>4</sup> or relativistic energy corrections.<sup>5</sup> Even when computing nonrelativistic energies, incorporation of these derivative discontinuities in trial wave functions greatly reduces the necessary number of variational parameters.<sup>6</sup> Indeed, the absence of an adequate description of electron-electron cusps is responsible for the slow convergence of standard orbital-based methods with basis size<sup>7,8</sup> and the increasingly popular explicitly correlated methods were developed to overcome this problem.<sup>9-14</sup>

Fournais *et al.* have sharpened Kato's cusp condition to include the effect of three-particle coalescence.<sup>15</sup> Expressing the fixed nucleus configurational wave function as  $\psi = e^F \phi$ , Fournais *et al.* proved, that the first order partial derivatives of  $\phi$  are everywhere continuous if

$$F = - \sum_{I=1}^N \sum_{i=1}^n Z_I r_{iI} + \frac{1}{2} \sum_{i \leq j=1}^n r_{ij} + C_0 \sum_{I=1}^N \sum_{i \leq j=1}^n Z_I \mathbf{r}_{iI} \cdot \mathbf{r}_{jI} \times \ln(r_{iI}^2 + r_{jI}^2), \quad (2)$$

where  $C_0 = (2 - \pi)/6\pi$  and  $I$  runs over the  $N$  nuclei and  $i, j$  run over the  $n$  electrons. The logarithmic terms arise to satisfy the three-particle singularity at the coalescence of a nucleus and two electrons. Indeed, terms of this type were first proposed by Fock<sup>16</sup> and have been confirmed to be numerically important for helium by Myers *et al.*<sup>17</sup> Although the results of Fournais *et al.* may be viewed as conditions on the second order derivatives at the singularities, they do not determine the structure of the wave function to quadratic  $r_{12}$  dependence, away from the nuclear positions. Furthermore, the first order partial derivatives of  $\psi$  itself are continuous at singularities where the wave function is zero and the above Jastrow factor  $e^F$  does not determine the form of the wave function close to these points. For regions of the configuration space that are away from three-particle coalescence, Pack and Byers Brown<sup>18</sup> derived the coalescence condition valid for  $\psi=0$  as follows:

$$\widetilde{\left. \frac{\partial^2 \psi}{\partial r_{12}^2} \right|}_{r_{12}=0} = \gamma \widetilde{\left. \frac{\partial \psi}{\partial r_{12}} \right|}_{r_{12}=0}, \quad (3)$$

where  $\gamma$  is the same as for Eq. (1) and the superscript on the tilde denotes a spherical average weighted with a spherical harmonic  $Y_{1m}$ . In addition, they generalized this and Kato's result beyond the fixed nuclei approximation, where  $\gamma$  is then given by  $Z_1 Z_2 \mu$ ,  $\mu$  being the reduced mass of the coalescing particles. The integrated forms of Eqs. (1) and (3) are

$$\psi = \psi_{r_{12}=0} (1 + \gamma r_{12}) + \mathbf{r}_{12} \cdot \mathbf{a} + \mathcal{O}(r_{12}^2), \quad (4)$$

<sup>a)</sup>Electronic mail: david.tew@chem-bio.uni-karlsruhe.de. FAX: +49-721-6083319.

$$\psi = \mathbf{r}_{12} \cdot \left. \frac{\partial \psi}{\partial \mathbf{r}_{12}} \right|_{r_{12}=0} \left( 1 + \frac{\gamma}{2} r_{12} \right) + \mathbf{r}_{12} \cdot \mathbf{b} \cdot \mathbf{r}_{12} + \mathcal{O}(r_{12}^3). \quad (5)$$

Pack and Byers Brown showed that the vector function  $\mathbf{a}$  and the traceless tensor function  $\mathbf{b}$  vanish for identical particle coalescence and noted that the spherical average in Eq. (1) is not necessary for this case. In this work, we extend the results of Pack and Byers Brown and examine the structure of the exact wave function to second and higher orders in the interparticle separation, deriving general expressions valid for the coalescence of any two charged particles with finite mass. We hope that a detailed understanding of the higher order  $r_{12}$  terms will lead to refinements of trial function forms and a further reduction of the number of variational parameters. We are particularly interested in improving the design of correlation factors, both for use in Jastrow-type wave functions and for the R12 class of methods, where orbital-based wave functions are augmented with terms that depend explicitly on the interparticle separation. This paper is organized as follows: In Sec. II, we present our extension of the analysis of Pack and Byers Brown and discuss the structure of the exact wave function and one- and two-particle density matrices. In Sec. III, we apply our analysis to orbital-based approaches, discussing the implications for Jastrow-type and R12 methods.

## II. GENERAL THEORY

In atomic units, the nonrelativistic, time-independent Schrödinger equation for a system of any  $n$  charged particles with charges  $Z_i$  and masses  $m_i$ , in the absence of an external field, is

$$\left( -\sum_{i=1}^n \frac{\nabla_i^2}{2m_i} + \sum_{i>j=1}^n \frac{Z_i Z_j}{r_{ij}} \right) \Psi = E \Psi. \quad (6)$$

The wave function  $\Psi$  is a function of the  $3n$  configurational degrees of freedom  $\mathbf{r}_1, \dots, \mathbf{r}_n$  and the  $n$  spin degrees of freedom  $\sigma_1, \dots, \sigma_n$ . An admissible  $\Psi$  must simultaneously satisfy Eq. (6) and the total spin eigenvalue equation, while exhibiting the correct Pauli symmetry upon the permutation of the coordinates of any two identical particles. It is well known that the full space-spin wave function can be constructed from linear combinations of appropriate degenerate spin-free eigenfunctions of Eq. (6),  $\psi(\mathbf{r}_1, \dots, \mathbf{r}_n)$ .<sup>19,20</sup> The coalescence conditions on the full wave function apply to each of the degenerate spin-free eigenfunctions and in the following analysis we consider these spatial functions.

We are interested in the region of configuration space where particles 1 and 2 are close together and all other particles are well separated from these two and from each other:  $0 \leq r_{12} \leq \epsilon$  and  $r_{i1}, r_{i2}, r_{ij} \gg \epsilon$  for  $i, j=3, n$ . We follow the analysis of Pack and Byers Brown.<sup>18</sup> We transform the space fixed position coordinates  $\mathbf{r}_1, \mathbf{r}_2$  to the center of mass and relative coordinates,  $\mathbf{s} = (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2)/M$  and  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ , where  $M = m_1 + m_2$ . The kinetic energy operator becomes

$$-\frac{\nabla_s^2}{2M} - \frac{\nabla_r^2}{2\mu} - \sum_{i=3}^n \frac{\nabla_i^2}{2m_i}, \quad (7)$$

where  $\mu = m_1 m_2 / M$ . In order to express the potential operator in terms of  $\mathbf{s}$  and  $\mathbf{r}$ , we introduce the cosines  $\cos \theta_i$ , between the vectors  $\mathbf{r}_{is} = \mathbf{r}_i - \mathbf{s}$  and  $\mathbf{r}$ . In terms of these cosines, the scalars  $r_{i1}$  and  $r_{i2}$  may be expressed as

$$r_{i1}^2 = r_{is}^2 + \left( \frac{m_2}{M} \right)^2 r^2 - 2 \frac{m_2}{M} r_{is} r \cos \theta_i, \quad (8)$$

$$r_{i2}^2 = r_{is}^2 + \left( \frac{m_1}{M} \right)^2 r^2 + 2 \frac{m_1}{M} r_{is} r \cos \theta_i. \quad (9)$$

In the region of interest, the potential terms involving  $r_{i1}$  and  $r_{i2}$  may be replaced with partial wave expansions in terms of Legendre polynomials  $P_l$  of the cosines as follows

$$\frac{1}{r_{i1}} = \frac{1}{r_{is}} \sum_{l=0}^{\infty} \left( \frac{m_2 r}{M r_{is}} \right)^l P_l(\cos \theta_i). \quad (10)$$

The expression for  $1/r_{i2}$  is similarly defined, replacing 1 with 2, and  $\cos \theta_i$  with  $-\cos \theta_i$ . The Legendre polynomials have the symmetry property  $P_l(-z) = (-1)^l P_l(z)$ . The full Schrödinger equation becomes

$$\left( -\frac{\nabla_s^2}{2M} - \frac{\nabla_r^2}{2\mu} - \sum_{i=3}^n \frac{\nabla_i^2}{2m_i} + \frac{Z_1 Z_2}{r} + \sum_{i>j=3}^n \frac{Z_i Z_j}{r_{ij}} + \sum_{i=3}^n \frac{Z_i}{r_{is}} \sum_{l=0}^{\infty} \left[ Z_1 \left( \frac{m_2 r}{M r_{is}} \right)^l + Z_2 \left( \frac{-m_1 r}{M r_{is}} \right)^l \right] P_l(\cos \theta_i) \right) \psi = E \psi. \quad (11)$$

Each term is straightforwardly assigned an order in  $\epsilon$  and we consider the Hamiltonian terms of order less than or equal to zero, where only spherically symmetric potential terms arise,

$$\left( -\frac{\nabla_r^2}{2\mu} + \frac{Z_1 Z_2}{r} + \hat{S} + \mathcal{O}(\epsilon) \right) \psi = E \psi. \quad (12)$$

$\hat{S}$  is independent of  $r$  (zeroth order in  $\epsilon$ ),

$$\hat{S} = -\frac{\nabla_s^2}{2M} - \sum_{i=3}^n \frac{\nabla_i^2}{2m_i} + \sum_{i>j=3}^n \frac{Z_i Z_j}{r_{ij}} + \sum_{i=3}^n \frac{Z_i}{r_{is}} [Z_1 + Z_2]. \quad (13)$$

The leading term in  $\mathcal{O}(\epsilon)$  is

$$\sum_{i=3}^n \frac{Z_i}{r_{is}} \left[ Z_1 \frac{m_2 r}{M r_{is}} - Z_2 \frac{m_1 r}{M r_{is}} \right] \cos \theta_i, \quad (14)$$

which cancels if particles 1 and 2 are equivalent. Pack and Byers Brown considered the terms in Eq. (12) that contribute to less than zeroth order and derived the first order coalescence conditions, which ensure that the singularity that arises in the potential at  $r=0$  is exactly canceled by a singularity in the kinetic energy. Their arguments generalize to include the zero order term. The most general bound solution to Eq. (12) may be written as

$$\psi(\mathbf{r}, \mathbf{s}, \mathbf{r}_3, \dots, \mathbf{r}_n) = \sum_{l=0}^{\infty} \sum_{m=-l}^l r^l f_{lm}(r, \mathbf{s}, \mathbf{r}_3, \dots, \mathbf{r}_n) Y_{lm}(\theta, \varphi), \quad (15)$$

where  $r$ ,  $\theta$ , and  $\varphi$  are the spherical polar coordinates of  $\mathbf{r}$  and the  $Y_{lm}$  are the spherical harmonics. Substitution into Eq. (12) yields

$$\sum_{l=0}^{\infty} \sum_{m=-l}^l r^l \left( \frac{1}{2\mu} \left[ \frac{\partial^2}{\partial r^2} + \frac{2(l+1)}{r} \frac{\partial}{\partial r} \right] - \frac{Z_1 Z_2}{r} - \hat{S} + E - \mathcal{O}(\epsilon) \right) f_{lm} Y_{lm} = 0. \quad (16)$$

Due to the linear independence of the  $Y_{lm}$ , the equality must hold for all  $l$  and  $m$ . Since  $\psi$  is analytic, except at the Coulomb singularities, we may expand the  $f_{lm}$  as a Taylor series in  $r$  up to some order  $v$

$$f_{lm}(s, r, \mathbf{r}_3, \dots, \mathbf{r}_n) = \sum_{k=0}^v r^k f_{lm}^k(s, \mathbf{r}_3, \dots, \mathbf{r}_n) \quad (17)$$

and equate each power of  $r$  (order of  $\epsilon$ ) to zero individually, which gives

$$\sum_{k=0}^v (k(k+2l+1)f_{lm}^k - 2\gamma f_{lm}^{k-1} - 2\mu(\hat{S}-E)f_{lm}^{k-2} - 2\mu\mathcal{O}(\epsilon^0)f_{lm}^{k-3})r^{k-2} = 0, \quad (18)$$

where  $\gamma = Z_1 Z_2 \mu$  and  $f_{lm}^0 \neq 0$ . Thus,

$$f_{lm}^1 = \frac{\gamma}{(l+1)} f_{lm}^0, \quad (19)$$

$$f_{lm}^2 = \frac{\mu}{(2l+3)} \left( \frac{\gamma^2}{\mu(l+1)} + \hat{S} - E \right) f_{lm}^0. \quad (20)$$

For equivalent particles,  $f_{lm}^3$  is also determined

$$f_{lm}^3 = \frac{\mu\gamma(3l+4)}{3(l+1)(2l+3)(l+2)} \left( \frac{\gamma^2}{\mu(3l+4)} + \hat{S} - E \right) f_{lm}^0. \quad (21)$$

Equation (19) is the first order coalescence condition as derived by Pack and Byers Brown. Equations (20) and (21) are second and third order coalescence conditions and are new. Note that the conditions apply to every  $f_{lm}$ , which belong to the spherical harmonic  $Y_{lm}$  for the relative angular momentum of the coalescing particles. The above coalescence conditions may be cast in differential form by identifying

$$f_{lm}^0 = \frac{1}{l!} \left. \frac{\partial^l \psi}{\partial r^l} \right|_{r=0}. \quad (22)$$

The tilde with superscript  $l$  denotes a weighted average over a sphere around the coalescence point, with weighting function  $Y_{lm}$ . Equation (19) may then be written as

$$\left. \frac{\partial^{l+1} \psi}{\partial r^{l+1}} \right|_{r=0} = \gamma \left. \frac{\partial^l \psi}{\partial r^l} \right|_{r=0}. \quad (23)$$

The conditions of Kato (1) and Pack and Byers Brown (3) correspond to  $l=0$  and 1, respectively. For  $l=0$ , there is a

discontinuity in the first order derivative and for  $l=1$  the discontinuity is in the second order derivative. Equations (20) and (21) represent conditions on the higher order derivatives of  $\psi$  as follows:

$$\left. \frac{\partial^{l+k} \psi}{\partial r^{l+k}} \right|_{r=0} = \frac{(l+k)!}{l!} c_l^k (b_l^k + \hat{S} - E) \left. \frac{\partial^l \psi}{\partial r^l} \right|_{r=0}, \quad (24)$$

with  $k=2$  and  $k=3$ , respectively. Only the  $k=3$  case results in a derivative discontinuity. It should be noted that these formulas only apply to terms in  $\psi$  up to  $\mathcal{O}(r^{l+2})$ , or  $\mathcal{O}(r^{l+3})$  for identical particles, where  $l$  is the lowest for which  $f_{lm}^0 \neq 0$ . To determine terms of higher order, coupling between the  $f_{lm}$  must be accounted for.

The new conditions (20) and (21), or equivalently Eq. (24), contain a contribution that is a simple multiple of  $f_{lm}^0$  and a term that is determined by the operation of  $\hat{S}-E$  on  $f_{lm}^0$ . The former is independent of the system, depending only on the nature of the particles, whereas the latter is system and state dependent and varies throughout configuration space. The presence of  $\hat{S}-E$  clearly prevents *a priori* knowledge of the exact eigenfunctions. However, an understanding of the correct structure is certainly beneficial for constructing trial functions. We give details of the general form of  $\psi$  before addressing the operator  $\hat{S}-E$ . The general form of the exact wave function is obtained by substituting the expressions for  $f_{lm}^1$  and  $f_{lm}^2$  (and  $f_{lm}^3$  if the coalescing particles are equivalent) into the wave function expansion of Eqs. (15) and (17).

$$\begin{aligned} \psi = & r^l \sum_{m=-l}^l Y_{lm} [1 + c_l^1 r \\ & + c_l^2 r^2 (b_l^2 + \hat{S} - E) + c_l^3 r^3 (b_l^3 + \hat{S} - E)] f_{lm}^0 \\ & + r^{l+1} \sum_{m=-(l+1)}^{l+1} Y_{l+1m} [1 + c_{l+1}^1 r \\ & + c_{l+1}^2 r^2 (b_{l+1}^2 + \hat{S} - E)] f_{l+1m}^0 \\ & + r^{l+2} \sum_{m=-(l+2)}^{l+2} Y_{l+2m} [1 + c_{l+2}^1 r] f_{l+2m}^0 + \mathcal{O}(r^{l+4}). \end{aligned} \quad (25)$$

The value of  $l$  is determined from the condition that  $f_{lm}^0 \neq 0$  and for nonequivalent particles, the equation is only valid to  $\mathcal{O}(r^{l+2})$ . All odd powers of  $r$  in the square brackets of Eq. (25) represent derivative discontinuities in the wave function at the singularity. It may be readily verified that Eq. (25) gives the correct expansion for hydrogenic wave functions at the nucleus. For electron-nucleus coalescence in many-electron systems, the lowest  $l$  for which  $f_{lm}^0 \neq 0$  is  $l=0$ , except for certain excited states where the electron density at the nucleus is zero. For electron-electron coalescence, we must differentiate between singlet and triplet spin coupled electron pairs: For singlet pairs, the spatial function is symmetric with respect to permutation of the electron configurations and only  $Y_{lm}$  with even  $l$  can contribute; for triplet pairs, only odd  $l$  contribute. The lowest relative angular momentum of the two singlet coupled electrons for which  $f_{lm}^0 \neq 0$  is  $l=0$  (unless the coalescence point happens to be at a node, in which case  $l=2$ , as discussed by Kutzelnigg and

TABLE I. Coefficients in Eq. (25) for two-particle coalescence involving electrons (e), nuclei (n), and positrons (p).

Case	$l$	$c_l^1$	$c_l^2$	$b_l^2$	$c_l^3$	$b_l^3$	$c_{l+1}^1$	$c_{l+2}^1$
e-n	0	$-\mu Z$	$\frac{1}{3}\mu$	$\mu Z^2$			$-\frac{1}{2}\mu Z$	
e-e	0	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{1}{18}$	$\frac{1}{8}$		$\frac{1}{6}$
e-e	1	$\frac{1}{4}$	$\frac{1}{10}$	$\frac{1}{4}$	$\frac{14}{720}$	$\frac{1}{14}$		$\frac{1}{8}$
e-p	0	$-\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{2}$				$-\frac{1}{4}$

Morgan<sup>21</sup>). For triplet pairs, there is a Fermi node at coalescence and  $l=1$ . Thus there is always a relative angular momentum of two electrons with the same spin, near the coalescence point. The structure of the wave function close to electron-positron coalescence is very similar to that of electron-nucleus coalescence, with  $l=0$  and every spherical harmonic contributing. In Table I, we have listed the values of  $c_l^k$  and  $b_l^k$  for these common situations in molecular physics.

The structure of the exact  $p$ -particle spinless reduced density matrix,  $\Gamma_p$ , is also of interest,

$$\begin{aligned} \Gamma_p(\mathbf{r}'_{\mathbf{p}}, \mathbf{r}_{\mathbf{p}}) &= \binom{n}{p} \int d\mathbf{r}_{\mathbf{q}} d\sigma_{\mathbf{p}} d\sigma_{\mathbf{q}} \Psi^*(\mathbf{r}'_{\mathbf{p}} \sigma_{\mathbf{p}}, \mathbf{r}_{\mathbf{q}} \sigma_{\mathbf{q}}) \Psi(\mathbf{r}_{\mathbf{p}} \sigma_{\mathbf{p}}, \mathbf{r}_{\mathbf{q}} \sigma_{\mathbf{q}}), \end{aligned} \quad (26)$$

where the subscripts  $\mathbf{p}$  and  $\mathbf{q}$  denote electrons  $1 \cdots p$  and  $p+1 \cdots n$ , respectively. We confine our discussion to the fixed nucleus approximation. Bingel has derived formulas to first order in  $r$  for the spinless one- and two-particle reduced density matrices.<sup>22,23</sup>

$$\Gamma_1(\mathbf{r}', \mathbf{r}) = \Gamma_1(\mathbf{r}', 0)(1 - Zr) + n\mathbf{A}^*(\mathbf{r}') \cdot \mathbf{r} + \mathcal{O}(r^2) \quad (27)$$

$$\begin{aligned} &= \Gamma_1(0, 0)(1 - Zr' - Zr) + n\mathbf{r}' \cdot \mathbf{A}(0) \\ &\quad + n\mathbf{A}^*(0) \cdot \mathbf{r} + \mathcal{O}(r'^2, r^2), \end{aligned} \quad (28)$$

where  $\mathbf{A}^*(\mathbf{r}') = \int d\mathbf{r}_{\mathbf{q}} d\sigma' d\sigma_{\mathbf{q}} \Psi^*(\mathbf{r}' \sigma', \mathbf{r}_{\mathbf{q}} \sigma_{\mathbf{q}}) \mathbf{a}(\sigma', \mathbf{r}_{\mathbf{q}} \sigma_{\mathbf{q}})$  and  $\mathbf{a}$  is equivalent to that of Eq. (4), except that here it depends on spin.<sup>22,24</sup>

$$\begin{aligned} \Gamma_2(\mathbf{r}' \mathbf{r}'_2, \mathbf{r} \mathbf{r}_2) &= \Gamma_2(\mathbf{r}' \mathbf{r}'_2, 0 \mathbf{r}_2)(1 - Zr) \\ &\quad + \frac{1}{2}n(n-1)\mathbf{A}^*(\mathbf{r}' \mathbf{r}'_2, \mathbf{r}_2) \cdot \mathbf{r} + \mathcal{O}(r^2), \quad (29) \\ &= \Gamma_2(0 \mathbf{r}'_2, 0 \mathbf{r}_2)(1 - Zr' - Zr) \\ &\quad + \frac{1}{2}n(n-1)\mathbf{r}' \cdot \mathbf{A}(\mathbf{r}'_2, 0 \mathbf{r}_2) \\ &\quad + \frac{1}{2}n(n-1)\mathbf{A}^*(0 \mathbf{r}'_2, \mathbf{r}_2) \cdot \mathbf{r} + \mathcal{O}(r'^2, r^2), \end{aligned} \quad (30)$$

with

$$\begin{aligned} \mathbf{A}^*(\mathbf{r}' \mathbf{r}'_2, \mathbf{r}_2) &= \int d\mathbf{r}_{\mathbf{q}} d\sigma' d\sigma'_2 d\sigma_{\mathbf{q}} \Psi^*(\mathbf{r}' \mathbf{r}'_2 \sigma' \sigma'_2, \mathbf{r}_{\mathbf{q}} \sigma_{\mathbf{q}}) \\ &\quad \times \mathbf{a}(\mathbf{r}_2 \sigma_2, \mathbf{r}_{\mathbf{q}} \sigma_{\mathbf{q}}). \end{aligned}$$

To obtain these equations, Bingel simply inserted the integrated form of Kato's cusp conditions into Eq. (26), implicitly assuming that configurations where more than two particles coalesce, which are included in the integration, do not contribute to first order. Using the fact that  $\psi = e^F \phi$ , where  $F$  is given in Eq. (2), we may verify that integration over the region of the coalescence of a singlet electron pair and a nucleus leads to terms of  $\mathcal{O}(r^2)$  [note that the first order partial derivatives of  $\phi$  are continuous and no terms of  $\mathcal{O}(r)$  in interparticle separations are present]. Furthermore, since there is a Fermi node at all higher order coalescence points, the first order partial derivatives of the wave function are continuous and these singularities introduce terms of  $\mathcal{O}(r^2)$  at worst. Therefore Bingel's formulas for the nuclear cusp of one- and two-particle spinless reduced density matrices are correct. To the author's knowledge, no formulas have yet been presented for electron-electron coalescence of singlet and triplet pairs. This omission is somewhat surprising and we therefore present the formula here. It is always possible to separate the wave function into two contributions  $\Psi = \Psi^+ + \Psi^-$ , where electrons 1 and 2 are singlet or triplet spin coupled, respectively.<sup>25</sup> Integration over all spin coordinates decouples the two-particle density matrix into

$$\Gamma_2(\mathbf{r}' \mathbf{r}'_2, \mathbf{r}_1 \mathbf{r}_2) = \Gamma_2^+(\mathbf{r}' \mathbf{r}'_2, \mathbf{r}_1 \mathbf{r}_2) + \Gamma_2^-(\mathbf{r}' \mathbf{r}'_2, \mathbf{r}_1 \mathbf{r}_2). \quad (31)$$

Transforming to the center of mass and relative coordinates and inserting Eq. (25), we obtain

$$\Gamma_2^+(\mathbf{r}' \mathbf{r}'_2, \mathbf{s} \mathbf{r}) = \Gamma_2^+(\mathbf{r}' \mathbf{r}'_2, \mathbf{s} 0) \left(1 + \frac{1}{2}r\right) + \mathcal{O}(r^2), \quad (32)$$

$$\Gamma_2^+(\mathbf{s}' \mathbf{r}', \mathbf{s} \mathbf{r}) = \Gamma_2^+(\mathbf{s}' 0, \mathbf{s} 0) \left(1 + \frac{1}{2}r' + \frac{1}{2}r\right) + \mathcal{O}(r'^2, r^2), \quad (33)$$

$$\Gamma_2^-(\mathbf{r}' \mathbf{r}'_2, \mathbf{s} \mathbf{r}) = \left. \frac{\partial \Gamma_2^-}{\partial \mathbf{r}} \right|_{r=0} \cdot \mathbf{r} \left(1 + \frac{1}{4}r\right) + \mathcal{O}(r^3), \quad (34)$$

$$\begin{aligned} \Gamma_2^-(\mathbf{s}' \mathbf{r}', \mathbf{s} \mathbf{r}) &= \mathbf{r}' \cdot \left. \frac{\partial^2 \Gamma_2^-}{\partial \mathbf{r}' \partial \mathbf{r}} \right|_{r=r'=0} \cdot \mathbf{r} \left(1 + \frac{1}{4}r' + \frac{1}{4}r\right) \\ &\quad + \mathcal{O}(r'^3, r^3). \end{aligned} \quad (35)$$

The structure of the higher order terms in  $r$  may be inferred from that of Eq. (25). Our analysis is insufficient to determine the system dependent operator that characterizes the  $\mathbf{s}$  dependence of these terms because the decoupling of the  $Y_{lm}$  in our derivation is only valid for  $r_{qs} > r$ . A more general analysis that treats three-particle coalescence points would be required.

Let us now turn to the system, state, and configuration dependence of the  $\hat{S}-E$  terms in Eq. (25). The operator  $\hat{S}$  describes the first order damping of the Coulomb interaction between the coalescing particles with the rest of the system. It contains the electrostatic interaction of the coalesced particles with the rest of the system, as well as kinetic and potential terms for the coordinates  $\mathbf{r}_3 \cdots \mathbf{r}_n$  and the kinetic energy of the center of mass coordinate. The combined op-

erator  $\hat{S}-E$  may be used to define an average screening length  $\lambda$  for a short range screened interaction  $e^{-r/\lambda}Z_1Z_2/r$ :  $Z_1Z_2/\lambda = \langle \psi | \hat{S}-E | \psi \rangle$ . In contrast to the derivative discontinuities, the effect of Coulombic screening is always present in orbital-based wave functions. Trial functions that combine orbitals with an explicit  $r$  dependence are a natural starting point for constructing approximate solutions with the correct structure to higher orders in  $r$ . The remainder of this paper focuses on attempts in this direction.

### III. ORBITAL-BASED TRIAL WAVE FUNCTIONS

In the following, we examine the Hartree–Fock (HF) wave function and Møller–Plesset (MP) correlated wave functions. We review the known first order dependence on  $r$  and discuss the second order terms, highlighting the approximate system, state, and configuration dependence. We compare the structure of these wave functions with that of the exact eigenfunctions and discuss how correlation factors may be used to improve the correlation treatment.

#### A. Hartree–Fock wave functions

The structure of the HF wave function at the nuclear cusp may be determined by examining the one-electron eigenvalue equation  $\hat{F}_1\phi_p(\mathbf{r}_1, \sigma_1) = \varepsilon_p\phi_p(\mathbf{r}_1, \sigma_1)$  for the canonical spin orbitals. Applying the arguments already presented, we find that the structure of the canonical orbitals at the nuclei is identically given by Eqs. (19) and (20), where  $\varepsilon_p$  replaces  $E$  and  $\hat{S}$  becomes

$$\hat{S}_1 = -\sum_{l=2}^N \frac{Z_l}{r_{1s}} + \sum_{j=1}^n \int d\mathbf{r}_2 d\sigma_2 \frac{\phi_j}{r_{2s}} (1 - \hat{P}_{12}) \phi_j. \quad (36)$$

The first order coalescence condition (19) is the same for the HF orbitals and the exact wave function and therefore all trial solutions constructed from exact HF orbitals satisfy the nuclear cusp explicitly. Since the Fock operator and the Kohn–Sham (KS) operator in density functional theory differ only in the exchange contribution, the KS density also trivially reproduces the exact nuclear cusp. The HF approximation to Eq. (20) is defined by replacing  $\hat{S}-E$  with  $\hat{S}_1-\hat{F}_1$ . The configurational dependence of the the second order coefficients is then easily computed since  $\hat{S}_1\phi_p = v_p\phi_p + \mathcal{O}(r_1)$ , where

$$v_p = -\sum_{l=2}^N \frac{Z_l}{r_{1s}} + \sum_{j=1}^n \int d\mathbf{r}_2 d\sigma_2 \frac{\phi_j}{r_{2s}} (\phi_j - f_{00}^{0,j}\phi_p/f_{00}^{0,p}), \quad (37)$$

and the constants  $f_{00}^{0,i}$  refer to the Taylor expansion (17) for spin-orbital  $\phi_j$ . The operator  $\hat{S}_1-\hat{F}_1$  accounts for the mean field electronic screening, but neglects the effect of correlation on the second order terms.

The structure of the HF wave function at electron-electron coalescence may be determined from the pair function eigenvalue equation  $(\hat{F}_1+\hat{F}_2)\Phi_{pq}^\pm = (\varepsilon_p+\varepsilon_q)\Phi_{pq}^\pm$ , where the orbital pair  $\phi_p\phi_q$  is singlet or triplet coupled to give the spatial functions  $\Phi_{pq}^+$  or  $\Phi_{pq}^-$ , respectively. It is always possible to express the restricted closed-shell HF determinants

such that in the constituent orbital products, each pair of electrons is either singlet or triplet coupled in this way and we confine our discussion to this case. The structure of the HF pair functions in the region of electron coalescence is given by

$$\sum_{k=0}^v (k(k+2l+1)f_{lm}^{k,pq^\pm} - (\hat{S}_0 - \varepsilon_p - \varepsilon_q)f_{lm}^{k-2,pq^\pm} - \mathcal{O}(\epsilon^0)f_{lm}^{k-4,pq^\pm})r^{k-2} = 0, \quad (38)$$

where  $f_{lm}^{k,pq^\pm}(s)$  refers to the Taylor expansion (17) for  $\Phi_{pq}^\pm$  and

$$\hat{S}_0 = -\frac{1}{4}\nabla_s^2 - \sum_{l=1}^N \frac{2Z_l}{r_{ls}} + \sum_{j=1}^{n/2} \int d\mathbf{r}_3 \frac{\chi_j}{r_{3s}} (4 - \hat{P}_{13} - \hat{P}_{23})\chi_j, \quad (39)$$

where  $\phi_p(\mathbf{r}_3, \sigma_3) = \chi_p(\mathbf{r}_3)\tau_p(\sigma_3)$ . Thus  $f_{lm}^{1,pq^\pm} = f_{lm}^{3,pq^\pm} = 0$  and

$$f_{lm}^{2,pq^\pm} = \frac{1}{2(2l+3)}(\hat{S}_0 - \varepsilon_p - \varepsilon_q)f_{lm}^{0,pq^\pm}. \quad (40)$$

The well known result that HF pair functions contain only even powers of  $r$  is manifest and no derivative discontinuities are present. The universal  $b_l^2$  term is also absent. All wave functions built from orbital pair functions alone exhibit the same deficiencies. Similarly, neither the HF nor the KS noninteracting two-particle reduced density matrices contain the linear  $r$  terms in Eqs. (32)–(35). In this HF approximation to Eq. (20), the operator  $\hat{S}-E$  is approximated with  $\hat{S}_0 - \hat{F}_1 - \hat{F}_2$ , where it should be noted that the exchange contribution to  $\hat{S}_0$  is nonlocal and couples all of the pair functions through

$$\int d\mathbf{r}_3 \frac{\chi_j}{r_{3s}} (\hat{P}_{13} + \hat{P}_{23})\chi_j f_{lm}^{0,pq^\pm} = \int d\mathbf{r}_3 \frac{\chi_j}{r_{3s}} (\chi_p f_{lm}^{0,jq^\pm} + \chi_q f_{lm}^{0,pj^\pm}). \quad (41)$$

#### B. Jastrow factors

Jastrow-type wave functions of the form  $e^J\Psi_{\text{HF}}$  play an important role as precursors to the fixed-node diffusion Monte Carlo method for treating electron correlation.<sup>26</sup> The Jastrow factor  $J$  should introduce the universal  $c_l^1$ ,  $b_l^2$ , and  $c_l^3$  terms, which are absent irrespective of whether or not the HF orbitals are allowed to relax. Recently, Scott *et al.* have demonstrated that the location of the nodes is linked to the first order coalescence conditions<sup>27</sup> and it is not unreasonable to assume that the higher order  $r$  dependence also has some bearing on the location of the nodes. Our analysis emphasizes the limitations of simple multiplicative choices for  $J$ . Since the  $c_l^1$  and  $c_{l+2}^1$  coefficients differ, it is not possible to satisfy the derivative discontinuities in both the  $f_{lm}$  and  $f_{l+2m}$  terms. Furthermore, it is only possible to simultaneously satisfy the singlet and triplet coalescence conditions if every pair of electrons of a given set of orbital products can be assigned as being singlet or triplet coupled. This is not usually attempted and instead the pairs are classified as  $\sigma\sigma$  or

$\alpha\beta$ . While it is correct to apply triplet coalescence conditions to  $\sigma\sigma$  pairs, it is not sufficient to simply apply the singlet coalescence conditions to  $\alpha\beta$  pairs, although this approach is certainly pragmatic.<sup>28</sup>

For the energetically dominant  $Y_{00}$  singlet case, comparing Eqs. (19)–(21) with the HF case suggests the choice  $J = \sum_{i<j} (\frac{1}{2}r_{ij} - \frac{1}{24}r_{ij}^2 + \mathcal{O}(r_{ij}^3))$ . The second order  $r$  dependence is then only lacking through the neglect of correlation in the screening operator and the energy  $\hat{S}_0 - \varepsilon_p - \varepsilon_q$ , which is dependent on the form of the orbitals used. To correct the third order  $r$  dependence, both the universal  $b_0^3$  term and the orbital-dependent term must be accounted for. Extending  $J$  by  $+\frac{1}{144}r_{ij}^3$  introduces  $b_0^3$ , but the correct  $c_0^3$  coefficient for the screening term cannot be obtained in this way and the  $r_{ij}^3$  term must therefore acquire a system, state, and configurational dependence equivalent to  $-\frac{1}{36}r^3(\hat{S}_0 - \varepsilon_p - \varepsilon_q)$ , if we neglect the effect of correlation on the screening operator and the energy. The analogous choice for the  $Y_{1m}$  triplet case is  $J = \sum_{i<j} (\frac{1}{4}r_{ij} - \frac{1}{160}r_{ij}^2 + \mathcal{O}(r_{ij}^3))$ , with  $+\frac{7}{2880}r_{ij}^3 - \frac{1}{180}r^3(\hat{S}_0 - \varepsilon_p - \varepsilon_q)$ .

### C. Møller–Plesset wave functions

The MP methods and the related coupled-cluster methods are the dominant wave function based treatments of electron correlation. Let us examine the first order perturbative correction  $u_{ij}^\pm$  to the spatial HF pair function  $\Phi_{ij}^\pm$  near electron coalescence.  $u_{ij}^\pm$  is strongly orthogonal to the set of occupied pair functions.<sup>29</sup> That is,  $u_{ij}^\pm = \hat{P}u_{ij}^\pm$ , where  $\hat{P}$  is the strong orthogonality projection operator.  $u_{ij}^\pm$  is given by<sup>29</sup>

$$(\hat{F}_1 + \hat{F}_2 - \varepsilon_i - \varepsilon_j)u_{ij}^\pm + \hat{P}\frac{1}{r_{12}}\Phi_{ij}^\pm = 0. \quad (42)$$

Let  $u_{ij}^\pm = \hat{P}w_{ij}^\pm$ , where  $w_{ij}^\pm$  does not satisfy the strong orthogonality requirements. Since  $[\hat{F}, \hat{P}] = 0$ , we may determine  $w_{ij}^\pm$  using the above equation, but removing the projection operator. Making the usual expansion for  $w_{ij}^\pm$ , we obtain

$$\sum_{k=0}^v (k(k+2l+1)w_{lm}^{k,ij\pm} - (\hat{S}_0 - \varepsilon_i - \varepsilon_j)w_{lm}^{k-2,ij\pm}) - \mathcal{O}(\epsilon^0)w_{lm}^{k-4,ij\pm} - f_{lm}^{k-1,ij\pm}r^{k-2} = 0. \quad (43)$$

Therefore the functions  $w_{lm}^{k,ij\pm}$  satisfy

$$w_{lm}^{1,ij\pm} = \frac{1}{2(l+1)}f_{lm}^{0,ij\pm}, \quad (44)$$

$$w_{lm}^{2,ij\pm} = \frac{1}{2(2l+3)}(\hat{S}_0 - \varepsilon_i - \varepsilon_j)w_{lm}^{0,ij\pm}, \quad (45)$$

$$w_{lm}^{3,ij\pm} = \frac{1}{6(l+2)}(\hat{S}_0 - \varepsilon_i - \varepsilon_j) \times \left( \frac{1}{2(2l+3)}f_{lm}^{0,ij\pm} + \frac{1}{2(l+1)}w_{lm}^{0,ij\pm} \right). \quad (46)$$

These conditions should be compared with Eqs. (19)–(21), which correspond to infinite order in the perturbation

parameter. The  $c_l^1$  derivative discontinuity appears to first order in the perturbation parameter, but the  $b_l^2$  and  $b_l^3$  terms are absent, occurring at second and third orders, respectively.

### D. R12 correlation factors

R12 explicitly correlated methods<sup>30</sup> augment the one-electron orbital basis with geminal functions of the form  $\hat{P}f(r)\Phi_{ij}^\pm$  to satisfy the  $c_l^1$  derivative discontinuity, often with  $f(r) = e^{-\zeta r}$ . Equation (44) is the known first order coalescence condition and has been used to predetermine the coefficients of the contributions of the geminal basis functions to the singlet and triplet pair functions in MP2 calculations,<sup>31</sup> which are  $-1/2\zeta$  and  $-1/4\zeta$ , respectively. Equations (45) and (46) may be used to determine appropriate values of  $\zeta$  for describing the short-range correlation. We argue that for this analysis the function  $f(r) = (1 - e^{-\zeta r})$  should be used.<sup>32</sup> Due to the projector  $\hat{P}$ , this only effects a sign change on the geminal basis. Expanding the functions  $\frac{1}{2\gamma(l+1)}(1 - e^{-\zeta r})f_{lm}^{ij\pm}$  to third order in  $r$ , we obtain

$$\left[ \frac{1}{2(l+1)}r - \frac{1}{2\gamma(l+1)}r^2 + \frac{1}{4(l+1)}r^3 \times \left( \frac{\gamma^2}{3} + \frac{1}{(2l+3)}(\hat{S}_0 - \varepsilon_i - \varepsilon_j) \right) \right] f_{lm}^{0,ij\pm}. \quad (47)$$

Equating the second and third order terms with Eqs. (45) and (46) and averaging over  $s$  lead to the following expressions for  $\zeta$  in singlet and triplet geminal functions:

$$\langle f_{00}^{0,ij+} | \zeta^2 + \frac{3}{4}\zeta + \frac{5}{6}(\hat{S}_0 - \varepsilon_i - \varepsilon_j) | f_{00}^{0,ij+} \rangle = 0, \quad (48)$$

$$\sum_{m=-1}^1 \langle f_{1m}^{0,ij-} | \zeta^2 + \frac{5}{12}\zeta + \frac{7}{15}(\hat{S}_0 - \varepsilon_i - \varepsilon_j) | f_{1m}^{0,ij-} \rangle = 0. \quad (49)$$

Values of  $\zeta$  determined by these expressions are appropriate for describing the short-range correlation in each pair function  $u_{ij}^\pm$ . Different values of  $\zeta$  are obtained for different orbital pairs. For coupled-cluster wave functions and higher orders of perturbation theory, the basis functions  $\hat{P}f(r)\Phi_{ij}^\pm$  are only appropriate to the extent that  $\psi \approx \psi_{\text{HF}}$ . Furthermore, basis functions of this form cannot simultaneously satisfy the  $c_l^1$  and  $c_{l+2}^1$  terms of the exact first order wave function. This deficiency could be removed by using additional geminal basis functions of the form  $\hat{P}f(r)Y_{2m}\Phi_{ij}^\pm$ .

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