I. INTRODUCTION

Universal features of the electronic wave function \( \Phi \) are of continued interest to physicists and chemists, as they guide the construction of highly accurate wave functions,\(^{10,11}\) explicitly correlated ansätze within F12 theory,\(^{12}\) and accurate Jastrow factors for quantum Monte Carlo (QMC) calculations.\(^{9,13}\) The Coulombic singularity at short interelectronic distances \( r_{12} = |r_1 - r_2| \) dominates all other terms and, near the two-particle coalescence (2PC) point \( r_{12} = 0 \), the behavior of \( \Phi \) becomes independent of other details of the system.

Early work by Kato,\(^{10}\) and elaborations by Pack and Byers-Brown,\(^{11}\) showed that, as two opposite-spin electrons approach, \( \Phi \) has the form

\[
\Phi = \left( 1 + \frac{r_{12}}{2} \right) \Phi(r_{12} = 0) + O(r_{12}^2). \tag{1}
\]

Similar 2PC conditions are known for triplet and unnatural parity singlet states.\(^{10,11}\)

To remove divergences in the local energy \( \Phi^{-1} \hat{H} \Phi \) at the 2PC points, cusp conditions such as \(^{(1)}\) must be satisfied. These divergences are especially harmful in diffusion QMC calculations, where they can lead to population-control problems and significant biases.\(^{10,11}\) Recently, several authors have further probed the coalescence behavior of the wave function, extending the analysis of Pack and Byers Brown to higher-order 2PC conditions.\(^{12,10,11}\) Surprisingly, imposing these additional conditions in QMC calculations was not found to be beneficial.\(^{10,11}\)

A wave function with correct 2PC behavior nonetheless yields a discontinuous local energy at three-particle coalescences (3PC), i.e. where \( r_{12} = r_{13} = r_{23} = 0 \). Unfortunately, a theoretical understanding of 3PC behavior has been much more elusive.\(^{10,11}\) In 1954, Fock\(^{12}\) rediscovered a result derived earlier by Gronwall\(^{20}\) and Bartlett.\(^{21}\) Using hyperspherical coordinates, he showed that, when both electrons approach the nucleus in a helium atom, the wave function takes the form

\[
\Phi = 1 - 2(r_1 + r_2) + \frac{r_{12}}{2} - \frac{\pi}{3\pi} r_1 \cdot r_2 \ln (r_1^2 + r_2^2) + \ldots \ . \tag{2}
\]

Such logarithmic terms are characteristic of 3PC behavior\(^{10-13}\) and using a wave function based on \(^{(2)}\) yields a continuous local energy for the helium atom.\(^{10}\)

The present work aims to elucidate the form of the wave function at three-electron coalescences for three electrons, in various spin states, confined to a harmonic potential in \( D = 2 \) or \( D = 3 \) dimensions. Eschewing the usual hyperspherical approach, we develop a new technique to show that, in each case, the wave function has non-analytical behavior characterized by a logarithmic term. Atomic units are used throughout.

II. THEORY

A system of three electrons, interacting coulombically but confined within a harmonic well, is variously called hookium, harmonium or Hooke’s law atom. It has been studied at high and low densities by Taut \textit{et al.}\(^{22,23}\) and Cioslowski \textit{et al.}\(^{24,25}\) The previous work of White and Stillinger\(^{26}\) and other work showing that the Kato cusp conditions are independent of the external potential\(^{22,24,25}\) imply that our 3PC results will also hold for any external potential.

The Hamiltonian of the system is

\[
\hat{H} = \frac{1}{2} \sum_{i=1}^{3} \left( -\nabla_i^2 + \omega^2 r_i^2 \right) + \kappa \sum_{i<j} \frac{1}{r_{ij}}, \tag{3}
\]

where \( \nabla_i^2 \) is the \( D \)-dimensional Laplacian for electron \( i \) and \( r_{ij} = |r_i - r_j| \) is the interelectronic distance between electrons \( i \) and \( j \). The strength of the interelectronic repulsion is measured by \( \kappa \). Without loss of generality, we choose the harmonic force constant \( \omega^2 = 1 \).

We consider only \( S \) states (i.e. \( L = 0 \)) and, after adopting Jacobi coordinates, the center-of-mass coordinate

\[
\sigma = (r_1 + r_2 + r_3)/\sqrt{3} \tag{4}
\]

separates and one can write

\[
\Psi(\sigma, \rho, \lambda) = \psi(\rho, \lambda, \rho \cdot \lambda) \Omega(\sigma), \tag{5}
\]
where

$$\rho = (r_1 - r_2)/\sqrt{2}, \quad \lambda = (2r_3 - r_1 - r_2)/\sqrt{6}$$ (6)

are the remaining Jacobi coordinates and

$$\Omega(\mathbf{r}) = \pi^{-D/4} \exp(-\sigma^2/2), \quad E_{\Omega} = D/2$$ (7)

are the wave function and energy of a harmonic oscillator.

If we express the rest of the Hamiltonian in terms of the interelectronic distances instead of $\rho$, $\lambda$ and $\rho \cdot \lambda$, then separation of variables reveals that the wave function $\psi$ in (3) is a solution of the Schrödinger-like equation

$$\left(\nabla^2 - 2\kappa U + 2\epsilon - V\right) \psi = 0,$$ (8)

where $\epsilon = E - E_{\Omega}$, the kinetic operator is

$$\nabla^2 = \frac{\partial^2}{\partial r_{12}^2} + \frac{D-1}{r_{12}} \frac{\partial}{\partial r_{12}} + \frac{r_{12}^2 + r_{13}^2 - r_{23}^2}{2r_{12}r_{13}} \frac{\partial^2}{\partial r_{12}\partial r_{13}} + \frac{\partial^2}{\partial r_{13}^2} + \frac{D-1}{r_{13}} \frac{\partial}{\partial r_{13}} + \frac{r_{13}^2 + r_{23}^2 - r_{12}^2}{2r_{13}r_{23}} \frac{\partial^2}{\partial r_{13}\partial r_{23}} + \frac{\partial^2}{\partial r_{23}^2} + \frac{D-1}{r_{23}} \frac{\partial}{\partial r_{23}} + \frac{r_{23}^2 + r_{12}^2 - r_{13}^2}{2r_{13}r_{23}} \frac{\partial^2}{\partial r_{13}\partial r_{23}},$$ (9)

and the internal and external potentials are

$$U = r_{12}^{-1} + r_{13}^{-1} + r_{23}^{-1}, \quad V = r_{12}^2 + r_{13}^2 + r_{23}^2.$$ (10a, 10b)

We also define the symmetric polynomials

$$s_1 = r_{12} + r_{13} + r_{23},$$ (11a)

$$s_2 = r_{12}r_{13} + r_{12}r_{23} + r_{13}r_{23},$$ (11b)

$$s_3 = r_{12}r_{13}r_{23},$$ (11c)

as well as the usual “hyperradius”

$$R = \sqrt{\frac{r_{12}^2 + r_{13}^2 + r_{23}^2}{3}},$$ (12)

and

$$\Delta = \sqrt{s_1(s_2 - 2r_{12})(s_2 - 2r_{13})(s_2 - 2r_{23})},$$ (13)

which is proportional to the area of the triangle defined by the three interelectronic distances. These quantities will be helpful for the remainder of this Communication.

We are interested in the behavior of $\psi$ when the $r_{ij}$ are all small and, because the Laplacian is $O(r_{ij}^{-2})$, we can treat $\kappa$ as a perturbation parameter. Expanding $\psi$ in ascending powers of $r_{ij}$ yields

$$\psi = \psi^{(0)} + \kappa \psi^{(1)} + \kappa^2 \psi^{(2)} + \ldots,$$ (14)

where the zeroth-, first- and second-order wave functions satisfy

$$\nabla^2 \psi^{(0)} = 0,$$ (15a)

$$\nabla^2 \psi^{(1)} = 2U \psi^{(0)},$$ (15b)

$$\nabla^2 \psi^{(2)} = 2U \psi^{(1)} - 2\epsilon \psi^{(0)}.$$ (15c)

The external potential $V$ does not contribute up to second order in $r_{ij}$ (or fourth-order perturbation theory).

### III. RESULTS

#### A. Doublet states

Following Pauncz and Matsen the wave function of an $S = 1/2$ state is given by

$$2\Phi = \frac{1}{\sqrt{3}} \left[ \alpha(1)\alpha(2)\beta(3)2\psi(r_1, r_2|r_3) - \alpha(1)\beta(2)\alpha(3)2\psi(r_1, r_3|r_2) - \beta(1)\alpha(2)\alpha(3)2\psi(r_3, r_2|r_1) \right],$$ (16)

where the vertical bar separates the spin-up and spin-down electrons, and the spatial wavefunction satisfies

$$2\psi(r_1, r_2|r_3) = -2\psi(r_2, r_1|r_3),$$ (17a)

$$2\psi(r_1, r_3|r_2) = 2\psi(r_1, r_3|r_2) + 2\psi(r_3, r_2|r_1).$$ (17b)

Equation (17a) ensures that the Pauli principle is satisfied and (17b) (which is found in Appendix C of Ref. [40]) ensures that there is no quartet contamination.

The zeroth-order wave function is the lowest solution of Eq. (15a) which satisfies (17a) and (17b) and, using the Frobenius method, one finds that

$$2\psi^{(0)} = r_{13}^2 - r_{23}^2.$$ (18)

In the same way, one finds the first-order wave function

$$2\psi^{(1)} = \frac{s_1}{D^2 - 1}(r_{13} - r_{23})(D_{13} + D_{23} - r_{12}).$$ (19)

Solving Eq. (15a) is difficult but it can be shown that

$$2\psi^{(2)} = 2N^{(2)} \ln(3R^2) 2\chi^{(2)} + O(R^4),$$ (20)

where

$$2\chi^{(2)} = (2r_{12}^2 - r_{13}^2 - r_{23}^2) 2\psi^{(0)}.$$ (21)

These zeroth-, first- and second-order wave functions agree with White and Stillinger’s hyperspherical 3D results.

The general second-order coefficient

$$N^{(2)} = \int 2U \psi^{(1)} \chi^{(2)} d\mathbf{n}$$ (22)

can be found by integrating over the hypersphere

$$n = \left(\frac{\rho^2 - \lambda^2}{R^2}, \frac{2 \rho \cdot \lambda}{R^2}, \frac{2 |\rho \times \lambda|}{R^2}\right)$$ (23)

of unit radius. In the 2D case, we find

$$2N^{(2)} = \frac{3\pi}{8} \left[ 3K(\frac{3}{2}) - 3E(\frac{3}{2}) - 114 K(\frac{1}{4}) + 130 E(\frac{1}{4}) \right] \approx 3.344854,$$ (24)

where $K(x)$ and $E(x)$ are the complete elliptic integrals of the first and second kind. In the 3D case, we find

$$2N^{(2)} = \frac{27\pi^2}{40} (11\sqrt{3} - 6\pi) \approx 1.352401,$$ (25)

which disagrees with White and Stillinger’s value.\[15]
B. Quartet states with $M_S = 1/2$

The 3PC behavior of quartet state wave functions has not been studied before. The wave function of an $S = 3/2$, $M_S = 1/2$ state is

$$4\Phi_{1/2} = \frac{1}{\sqrt{3}} \left[ (\alpha(1)\alpha(2))\beta(3) + (\alpha(1)\beta(2))\alpha(3) \right] 4\Psi(r_1, r_2, r_3)$$

(26)

where the spatial wave function is antisymmetric, i.e.

$$4\Psi(r_1, r_2, r_3) = +4\Psi(r_2, r_3, r_1) = +4\Psi(r_3, r_1, r_2) = -4\Psi(r_1, r_2, r_3)$$

(27)

and $\Psi$ is symmetric solution of (8) in dimension $D$.

Using the same approach as above, we seek antisymmetric zeroth- and first-order wave functions and find

$$4\psi^{(0)}_{1/2} = (r_{12}^2 - r_{13}^2)(r_{12}^2 - r_{23}^2)(r_{13}^2 - r_{23}^2)$$

(28)

and

$$4\psi^{(1)}_{1/2} = \frac{(r_{12} - r_{13})(r_{12} - r_{23})(r_{13} - r_{23})}{(D + 1)(D + 3)(D + 5)} \times (c_{020}s_2^2 + c_{101}s_1s_3 + c_{210}s_1^2s_2 - c_{400}s_1^4),$$

(29)

where

$$c_{020} = 8/5, \quad c_{101} = 3/5 - (D + 4)/(D + 6),$$

(30)

$$c_{210} = (D + 3)(D + 6) + \frac{2}{5}, \quad c_{400} = D + 3,$$

(31)

and $s_1$, $s_2$ and $s_3$ are given by (11). The second-order wave function is

$$4\psi^{(2)}_{1/2} = 4N_{1/2}^{(2)} \ln(3R^2) 4\chi_{1/2}^{(2)} + O(R^8),$$

(32)

where

$$4\chi_{1/2}^{(2)} = \frac{A(r_{12}^2r_{13}^2 + r_{12}^2r_{23}^2 + r_{13}^2r_{23}^2) - B\Delta^2}{r_{12}^2 + r_{13}^2 + r_{23}^2} 4\psi_{1/2}^{(0)}.$$  

(33)

and

$$A = \frac{D - 1}{D + 1}, \quad B = \frac{D + 5}{D + 1}.$$  

(34)

The differences between (32) and (33) are interesting. In particular, the second-order wave function of the quartet, unlike that of the doublet, is dimension-dependent, and the logarithmic singularity for the quartet appears at order $R^8 \ln R$, rather than $R^4 \ln R$. This agrees with the prediction by White and Stillinger[33] that the non-analytic terms for the quartet state are of higher order.

In the 2D case, we use (22) to find

$$4N_{1/2}^{(2)} = \frac{243\pi}{6522886} \left[ 48171 K(\frac{1}{4}) - 54572 E(\frac{1}{4}) \right] \approx 0.131306.$$  

(35)

In the 3D case, we find

$$4N_{1/2}^{(2)} = \frac{27\pi^2}{1280} \left[ 7641\sqrt{3} \frac{1}{501760} \right] \approx 0.165672.$$  

(36)

C. Quartet states with $M_S = 3/2$

The wave function of an $S = 3/2$, $M_S = 3/2$ state is given by

$$4\Phi_{3/2} = \alpha(1)\alpha(2)\alpha(3)D(r_1, r_2, r_3) 4\Psi(r_1, r_2, r_3),$$

(37)

where

$$D(r_1, r_2, r_3) = \left[ \begin{array}{c} x_1 & y_1 & 1 \\ x_2 & y_2 & 1 \\ x_3 & y_3 & 1 \end{array} \right]$$

(38)

and $4\Psi$ is a symmetric solution of (3) in dimension $D + 2$. This “interdimensional degeneracy” has been used many times in the past, especially to calculate the energy of excited states in atomic systems[34] See Refs. 36, 46, 47 and 39 for more details.

Using the Frobenius method as before, one finds that the zeroth- and first-order wave functions are

$$4\psi_{3/2}^{(0)} = 1, \quad 4\psi_{3/2}^{(1)} = \frac{s_1}{D + 1}.$$  

(39)

The second-order wave function has the form

$$4\psi_{3/2}^{(2)} = 4N_{3/2}^{(2)} \ln(3R^2) 4\chi_{3/2}^{(2)} + O(R^2),$$

(40)

where

$$4\chi_{3/2}^{(2)} = \frac{A(r_{12}^2r_{13}^2 + r_{12}^2r_{23}^2 + r_{13}^2r_{23}^2) - B\Delta^2}{r_{12}^2 + r_{13}^2 + r_{23}^2} 4\psi_{3/2}^{(0)},$$

and

$$A = \frac{D + 1}{D + 4}, \quad B = \frac{D + 5/2}{D + 4}.$$  

(41)

Though similar, the logarithmic singularities in the quartet states depend on $M_S$ via the constants in (34) and (42). In the 2D case, we use (22) to find

$$4N_{3/2}^{(2)} = \frac{9\pi^3}{32} \left[ 7E(\frac{3}{5}) - 3K(\frac{3}{5}) \right] \approx 1.834021.$$  

(43)

In the 3D case, we find

$$4N_{3/2}^{(2)} = \frac{3\pi^2}{35} \left( 15\sqrt{3} - 8\pi \right) \approx 0.717397.$$  

(44)

In Fig. 1, we have represented $(\psi_1 + \psi_2)/\psi_0$ for the 3D doublet and quartet states at the 3PC point for various arrangements.

IV. CONCLUSION

In this Communication, we have shown that the exact wave function at the three-electron coalescence point for
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FIG. 1. $(\psi_1 + \psi_2)/\psi_0$ at the vicinity of the 3PC for the 3D doublet and quartet states with collinear (left), equilateral (center) and isosceles (right) arrangements.

various spin states of three electrons in a two- or three-dimensional harmonic well diverges logarithmically. Our results should be valuable for explicitly correlated calculations and for QMC methods where the local energy discontinuity at the three-electron coalescence point could be removed by including logarithmic terms.

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