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Spin-Dependent Bohmian Electronic Trajectories for Helium

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Abstract We examine "de Broglie-Bohm" causal trajectories for the two electrons in a nonrelativistic helium atom, taking into account the spin-dependent momentum terms that arise from the Pauli current. Given that this many-body problem is not exactly solvable, we examine approximations to various helium eigenstates provided by a low-dimensional basis comprised of tensor products of one-particle hydrogenic eigenstates.

First to be considered are the simplest approximations to the ground and first-excited electronic states found in every introductory quantum mechanics textbook. For example, the trajectories associated with the simple $1s(1)1s(2)$ approximation to the ground state are, to say the least, nontrivial and nonclassical.

We then examine higher-dimensional approximations, i.e., eigenstates Ψ_α of the Hamiltonian in this truncated basis, and show that $\nabla_i S_\alpha = 0$ for both particles, implying that only the spin-dependent momentum term contributes to electronic motion. This result is independent of the size of the truncated basis set, implying that the qualitative features of the trajectories will be the same, regardless of the accuracy of the eigenfunction approximation.

The electronic motion associated with these eigenstates is quite specialized due to the condition that the spins of the two electrons comprise a two-spin eigenfunction of the total spin operator. The electrons either (i) remain stationary or (ii) execute circular orbits around the z-axis with constant velocity.

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1 Introduction

In this paper we investigate the nonrelativistic, spin-dependent "de Broglie-Bohm" causal trajectories [3, 8] for the two electrons of a helium atom. This work may be viewed as a continuation of earlier work on spin-dependent causal trajectories for the hydrogen atom, first in the nonrelativistic setting [4] and then for the Pauli and Dirac representations [5]. The helium atom represents a more complicated, yet still tractable, fermionic system that can be studied in terms of the causal interpretation of quantum mechanics. As well, the eigenfunction expansion approach adopted for the numerical calculations permits a qualitative analysis of the trajectories that would not be available from traditional mesh-based numerical methods for PDEs.

A few words on the de Broglie-Bohm causal interpretation and spin-dependent trajectories are in order. First, in David Bohm's original interpretation [2], the motion of a quantum particle is determined by its Schrödinger wavefunction Ψ which acts as a kind of "guidance wave". If the wavefunction is expressed in the form

$$\Psi(\mathbf{r},t) = R(\mathbf{r},t)e^{iS(\mathbf{r},t)/\hbar}, \tag{1}$$

where R and S are assumed to be real-valued, then under the Schrödinger theory the particle follows a trajectory through space given by the momentum field

$$\mathbf{p} \equiv m\frac{d\mathbf{r}}{dt} = \nabla S. \tag{2}$$

Excellent and comprehensive discussions of this interpretation are to be found in [3] and [8].

The Schrödinger equation, however, does not account for a particle's intrinsic angular momentum, or what is commonly referred to as particle spin. As readers are well aware, spin was introduced to account for the results of experiments involving the transmission of atoms through inhomogenous magnetic fields (for example, the Stern-Gerlach experiment). It was found that the splitting of energy levels due to the magnetic field could only be explained if the electron was assigned an intrinsic angular momentum of magnitude $\hbar/2$ [9]. Under the standard interpretation of quantum mechanics this intrinsic angular momentum is pictured as arising from an extended electron spinning about an axis through its center. The axis is referred to as the *spin vector* [1], having length $\hbar/2$, in accordance with the magnitude of the angular momentum it represents.

In [3], Bohm's original theory is extended to include particle spin. The authors find that the picture of an extended electron spinning about an axis through its center is inadequate in a causal scheme and violates Lorentz invariance. Instead, by taking the non-relativistic limit of the Dirac equation they arrive at the spin-dependent momentum field corresponding to (2),

$$\mathbf{p} \equiv m\frac{d\mathbf{r}}{dt} = \nabla S + \frac{1}{\rho}\nabla\rho \times \mathbf{s}. \tag{3}$$

Here, ρ is the usual (spatial) probability density function, and the particle spin vector $\mathbf{s}$ is defined as follows,

$$\mathbf{s} \equiv \frac{\hbar}{2\rho} \Psi^{\dagger} \sigma \Psi, \tag{4}$$

where σ is a 3-dimensional vector of Pauli spin-matrices and the wavefunction, Ψ, is a 2-component spinor. Notice from (3) that the effect of particle spin is to add a divergence-free contribution to the spin-independent Schrödinger momentum field, (2). Thus, in the Bohmian picture spin is not representative of an axis about which an extended particle rotates. Instead a Bohmian particle is a point particle which travels along trajectories given by (2) (for the spin-independent case) or (3) (for the spin-dependent case). Keeping this in mind, we will continue to refer to $\mathbf{s}$ as a "spin vector" even though it is not the spin vector associated with the standard interpretation. It is important to make this distinction.

Equation (3) was formulated for a single particle. In order to analyse the helium atom it must be recast for a many-body system. This is a simple procedure and we refer the reader to Sect. 10.5 of [3]. Here Bohm and Hiley take the non-relativisitic limit of the many-body Dirac equation to obtain the momentum fields,

$$\mathbf{p}_i \equiv m \frac{d\mathbf{r}_i}{dt} = \nabla_i S + \frac{1}{\rho} \nabla_i \rho \times \mathbf{s}_i, \tag{5}$$

where $\mathbf{p}_i$ and $\mathbf{r}_i$ are the momentum and position of the i-th particle, respectively, ∇_i represents the gradient with respect to the coordinates of the i-th particle and $\mathbf{s}_i$ is the spin vector of the i-th particle defined analogously to (4) by

$$\mathbf{s}_i \equiv \frac{\hbar}{2\rho} \Psi^{\dagger} \sigma_i \mathbf{1}_{i'} \Psi. \tag{6}$$

Here σ_i represents the Pauli spin-matrices acting on particle i and $\mathbf{1}_{i'}$ represents the identity matrix acting on the spin indices of all other particles.

Finally, we mention that an account of the various investigations of the causal interpretation, or even a listing of the major works, is quite beyond the scope of this paper. For this reason, we have not attempted to reference even a few of the many influential papers on the subject. For a most interesting and informative account, the reader is referred to the thought-provoking book by Cushing [7].

2 Constructing Approximate Electronic Wavefunctions of the Helium Atom

2.1 The Pauli Equation for Helium

Because of the role of spin, we must begin with the Pauli equation. The electronic wavefunction $\Psi_P(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2, t)$ of a nonrelativistic, spin-dependent, two-electron atom is given by the solution to the following time-dependent Pauli equation,

Table 1 Two-spin eigenfunctions $\Sigma^{S}_{S_z}(1,2)$ with associated spin vectors (in Cartesian coordinates) for each electron

Singlet state $S = 0$ (antisymmetric)		
$\Sigma^0_0 = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$	$\mathbf{s}_1 = (0, 0, 0)$	$\mathbf{s}_2 = (0, 0, 0)$
Triplet state $S = 1$ (symmetric)		
$\Sigma^1_1 = \alpha(1)\alpha(2)$	$\mathbf{s}_1 = (0, 0, \frac{\hbar}{2})$	$\mathbf{s}_2 = (0, 0, \frac{\hbar}{2})$
$\Sigma^1_0 = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$	$\mathbf{s}_1 = (0, 0, 0)$	$\mathbf{s}_2 = (0, 0, 0)$
$\Sigma^1_{-1} = \beta(1)\beta(2)$	$\mathbf{s}_1 = (0, 0, -\frac{\hbar}{2})$	$\mathbf{s}_2 = (0, 0, -\frac{\hbar}{2})$

$$i\hbar\frac{\partial\Psi_P}{\partial t} = \left(-\frac{\hbar^2}{2m_e}(\nabla_1 - ie\mathbf{A})^2 - \frac{\hbar^2}{2m_e}(\nabla_2 - ie\mathbf{A})^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} + \mu(\sigma_1\cdot\mathbf{B}) + \mu(\sigma_{\mathbf{2}}\cdot\mathbf{B})\right)\Psi_{\mathbf{P}}, \tag{7}$$

where m_e denotes the mass of the electron and Z the atomic number of the nucleus. Here, s_1 and s_2 denote the dependence of the wavefunction on the spins of the two electrons. We use the standard approximation of infinite nuclear mass so that the center of mass of the atom (which defines the origin) is at the nucleus for all time. **A** denotes the magnetic potential and the final two terms represent the interaction of the spins of each electron with the magnetic field, $\mathbf{B} = \nabla\times\mathbf{A}$.[1] Here we examine a free helium atom for which $Z = 2$ and $\mathbf{A} = \mathbf{B} = \mathbf{0}$. The Pauli equation then becomes

$$i\hbar\frac{\partial\Psi_P}{\partial t} = \left(-\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\right)\Psi_P. \tag{8}$$

Since the Hamiltonian in (8) is spin-independent, wavefunction Ψ_P can be factored as follows,

$$\Psi_P(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2, t) = \Psi(\mathbf{r}_1, \mathbf{r}_2, t)\Sigma(1,2). \tag{9}$$

Here, $\Sigma(1,2)$ denotes the two-particle spinor function which will contain the constant spin vectors.

It is well known that the spins of two spin-$\frac{1}{2}$ particles may be combined to form eigenfunctions of the total spin operator $\hat{S}$ that correspond to total spin $S = 0$ (singlet, $S_z = 0$) or $S = 1$ (triplet, $S_z = -1, 0, 1$). In this representation the spins of each electron are eigenstates of $\hat{S}_z$, the spin in the z-direction, and $\Sigma(1,2)$ is expressed in terms of the two-component vectors, $\alpha(i) = (1,0)^T_i$ and $\beta(i) = (0,1)^T_i$. The eigenfunctions and corresponding spin vectors (calculated according to (6)) are presented in Table 1. (A more detailed discussion is given in [11]).

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[1] This equation is an approximation which neglects the coupling between the spins of each electron, the coupling between the orbital angular momenta of the electrons and their spins and any dynamics associated with the nucleus (nuclear motion and nuclear spin). See [6] for a discussion of these terms.

Due to the Pauli exclusion principle, the two-electron total wavefunction Ψ_P must be antisymmetric with respect to interchange of the two electrons. As a result, the spatial and spin portions of Ψ_P in (9) must have *opposite parities* with respect to interchange of particles—for example, if Ψ is symmetric then Σ must be antisymmetric.

2.2 Approximations via Eigenfunction Expansions

As is well known, there is no exact, closed-form solution to (8). A standard practice for determining energies, polarizabilities, etc., is to construct accurate approximations to the desired electronic wavefunction by means of a Ritz-type variational procedure that employs a sufficiently large basis set of functions in the appropriate Hilbert space. In this study, we employ a rather straightforward variational method in which the electronic repulsion term is treated as a perturbation, i.e.,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}, \tag{10}$$

where

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}, \qquad \hat{H}^{(1)} = \frac{e^2}{r_{12}}, \tag{11}$$

and $Z = 2$ for helium. In what follows, we let $\psi_{nlm}(\mathbf{r})$ denote the usual hydrogenic eigenfunctions (see [10] for example) with energy eigenvalues,

$$E^{(0)}_{nlm} = -\frac{Z^2e^2}{2a_0n^2}, \quad n = 1, 2, \ldots, \tag{12}$$

where a_0 denotes the Bohr radius.

The eigenfunctions of $H^{(0)}$ have the form

$$\Psi^{(0)}_{ij}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n_il_im_i}(\mathbf{r}_1)\psi_{n_jl_jm_j}(\mathbf{r}_2), \tag{13}$$

with associated energy eigenvalues,

$$E^{(0)}_{ij} = E^{(0)}_{n_il_im_i} + E^{(0)}_{n_jl_jm_j}. \tag{14}$$

We assume an expansion of the two-electron time-dependent helium spatial wavefunction $\Psi(t)$ in terms of this unperturbed tensor product basis, i.e.,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} c_{ij}(t)\Psi^{(0)}_{ij}(\mathbf{r}_1, \mathbf{r}_2). \tag{15}$$

Substitution into (8) yields an infinite system of linear ordinary differential equations in the complex-valued coefficients $c_{ij}(t)$, which may be written in matrix form as

$$i\hbar\frac{d\mathbf{c}}{dt} = \mathbf{Ac} + \mathbf{Bc}. \tag{16}$$

The matrix **A** is real and diagonal, with entries $E^{(0)}_{ij}$. The matrix **B** is real and symmetric, representing the electronic interaction terms,

$$B_{ij,kl} = \left\langle \psi_{n_i l_i m_i}(\mathbf{r}_1)\psi_{n_j l_j m_j}(\mathbf{r}_2) \left| \frac{e^2}{r_{12}} \right| \psi_{n_k l_k m_k}(\mathbf{r}_1)\psi_{n_l l_l m_l}(\mathbf{r}_2) \right\rangle. \tag{17}$$

The matrix elements $B_{ij,kl}$ for the first few lowest hydrogenic eigenstates are tabulated in textbooks. Those for higher quantum numbers, however, were computed by means of the computer algebra software MAPLE. The values necessary for our restricted basis set are tabulated in Appendix.

In practical computations that involve standard software packages, including the ODE packages used in this study, it is convenient to decompose the complex expansion coefficients $c_{ij}(t)$ into real and imaginary parts, i.e., $c_{ij}(t) = a_{ij}(t) + ib_{ij}(t)$. The system in (16) then generates a pair of coupled (infinite-dimensional) first-order systems in the real coefficients $a_{ij}(t)$ and $b_{ij}(t)$:

$$\begin{aligned} \frac{d}{dt}a_{ij}(t) &= \frac{1}{\hbar}E^{(0)}_{ij}b_{ij}(t) + \frac{1}{\hbar}\sum_{k,l} B_{ij,kl}b_{kl}(t), \\ \frac{d}{dt}b_{ij}(t) &= -\frac{1}{\hbar}E^{(0)}_{ij}a_{ij}(t) - \frac{1}{\hbar}\sum_{k,l} B_{ij,kl}a_{kl}(t). \end{aligned} \tag{18}$$

Prescription of the initial values $a_{ij}(0)$ and $b_{ij}(0)$ will yield a unique solution that characterizes the time evolution of the wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ in (15).

2.3 Finite-Dimensional Approximations

In any practical implementation, the infinite eigenfunction expansion in (15) must be truncated. The primary goal of this study is to examine electronic trajectories for approximations to the ground state. In an effort to obtain reasonable approximations, but also to keep the calculations tractable, we have employed only hydrogenic eigenstates with principal quantum numbers $n = 1, 2$ and $m = 0$, that is, the following single-electron states $\psi_{n_i l_i m_i}$ in (13):

$$\begin{aligned} i = 1: &\quad (n_1, l_1, m_1) = (1, 0, 0) \quad (1s), \\ i = 2: &\quad (n_2, l_2, m_2) = (2, 0, 0) \quad (2s), \\ i = 3: &\quad (n_3, l_3, m_3) = (2, 1, 0) \quad (2p_0). \end{aligned} \tag{19}$$

This set yields nine tensor product functions $\Psi^{(0)}_{ij}$. It follows that the system of ODEs in (18) has dimension $9 + 9 = 18$. That being said, the procedure could easily be extended to include more hydrogenic basis functions if more accurate estimates of the ground state energy were desired. As we shall show, however, the qualitative behaviour of the Bohmian trajectories will remain the same.

3 Computation of Bohmian Trajectories from $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$

It now remains to compute the appropriate quantitites in the guidance equation (5) from the time-dependent wavefunction Ψ in (15). First, we express the guidance equation (5) in terms of Ψ as follows,

$$\mathbf{p}_i = \frac{\hbar}{2i\rho}[\Psi^*\nabla_i\Psi - \Psi\nabla_i\Psi^*] + \frac{1}{\rho}\nabla_i\rho \times \mathbf{s}_i, \tag{20}$$

where $\rho = \Psi^*\Psi = |\Psi|^2$.

Spin-independent term: It is convenient to write the first term in (20) as

$$\frac{\hbar}{2i\rho}[\Psi^*\nabla_i\Psi - \Psi\nabla_i\Psi^*] = \frac{\hbar}{\rho}\mathrm{Im}(\Psi^*\nabla_i\Psi). \tag{21}$$

In terms of the solutions to the linear system in (18), this term becomes (details are given in [11])

$$\begin{aligned}\frac{\hbar}{\rho}\mathrm{Im}(\Psi^*\nabla_i\Psi) = \frac{\hbar}{\rho}\sum_{g,h,j,k=1}^{3} &\big(a_{gh}(t)b_{jk}(t) - a_{jk}(t)b_{gh}(t)\big)\psi_g(\mathbf{r}_1)\psi_h(\mathbf{r}_2)\\ &\times\left\{A^i_{jk}(\mathbf{r}_1,\mathbf{r}_2)\hat{\mathbf{e}}_r + B^i_{jk}(\mathbf{r}_1,\mathbf{r}_2)\hat{\mathbf{e}}_\theta + C^i_{jk}(\mathbf{r}_1,\mathbf{r}_2)\hat{\mathbf{e}}_\psi\right\}.\end{aligned} \tag{22}$$

Here ψ_g and ψ_h are shorthand notations for the hydrogenic eigenstates $\psi_{n_g l_g m_g}$ and $\psi_{n_h l_h m_h}$, respectively (cf. (13)),

$$A^i_{jk}(\mathbf{r}_1,\mathbf{r}_2) = \begin{cases} \frac{\partial R_{n_j,l_j}(r_1)}{\partial r_1} Y_{l_j}(\theta_1,\phi_1) R_{n_k,l_k}(r_2) Y_{l_k}(\theta_2,\phi_2), & \text{if } i=1,\\ R_{n_j,l_j}(r_1) Y_{l_j}(\theta_1,\phi_1)\frac{\partial R_{n_k,l_k}(r_2)}{\partial r_2} Y_{l_k}(\theta_2,\phi_2), & \text{if } i=2,\end{cases} \tag{23}$$

$$B^i_{jk}(\mathbf{r}_1,\mathbf{r}_2) = \begin{cases} R_{n_j,l_j}(r_1)\frac{\partial Y_{l_j}(\theta_1,\phi_1)}{\partial\theta_1} R_{n_k,l_k}(r_2) Y_{l_k}(\theta_2,\phi_2), & \text{if } i=1,\\ R_{n_j,l_j}(r_1) Y_{l_j}(\theta_1,\phi_1) R_{n_k,l_k}(r_2)\frac{\partial Y_{l_k}(\theta_2,\phi_2)}{\partial\theta_2}, & \text{if } i=2,\end{cases} \tag{24}$$

and

$$C^i_{jk}(\mathbf{r}_1,\mathbf{r}_2) = 0 \quad \text{for } i = 1, 2. \tag{25}$$

The latter result follows from the fact that all of the hydrogenic eigenstates used in our calculations have no ϕ-dependence ($m = 0$). In the above expressions, $(n_1, n_2, n_3) = (1, 2, 2)$ and $(l_1, l_2, l_3) = (0, 0, 1)$ denote the quantum numbers employed in our computations.

Spin-dependent term: With regard to the second term in (20), it is convenient to use the fact that

$$\nabla_i\rho = \nabla_i(\Psi^*\Psi) = 2\mathrm{Re}(\Psi^*\nabla_i\Psi). \tag{26}$$

This yields the result

$$\frac{1}{\rho}\nabla_i \rho = \frac{2}{\rho}\sum_{g,h,j,k=1}^{3}\big(a_{gh}(t)a_{jk}(t)+b_{jk}(t)b_{gh}(t)\big)\psi_g(\mathbf{r}_1)\psi_h(\mathbf{r}_2) \times \left\{A^i_{jk}(\mathbf{r}_1,\mathbf{r}_2)\hat{\mathbf{e}}_r + B^i_{jk}(\mathbf{r}_1,\mathbf{r}_2)\hat{\mathbf{e}}_\theta + C^i_{jk}(\mathbf{r}_1,\mathbf{r}_2)\hat{\mathbf{e}}_\phi\right\}, \tag{27}$$

where the A^i_{jk}, B^i_{jk} and C^i_{jk} coefficients have already been defined in (23), (24) and (25), respectively.

The spin-dependent part of the momentum in (20) is then obtained by taking the cross product of the above vectors ($i = 1, 2$) with the corresponding spin vectors, $\mathbf{s}_i$. After expressing the spin vectors in spherical coordinates, (20) yields a total of six equations for the time-dependent momenta $\mathbf{p}_i(t) = m\dot{\mathbf{r}}_i(t)$ of the two electrons in spherical coordinates according to (3).

These differential equations, along with those for $a_{ij}(t)$ and $b_{ij}(t)$ in (18), are then integrated simultaneously to yield the trajectories $\mathbf{r}_i(t)$ of the electrons. The procedure is started by prescribing the following:

1. Initial conditions, $a_{ij}(0)$, $b_{ij}(0)$, defining the wavefunction $\Psi(\mathbf{r}_1,\mathbf{r}_2,0)$,
2. Initial positions, $\mathbf{r}_1(0)$, $\mathbf{r}_2(0)$, of the electrons.

Finally, we note that (22)–(25) and (27) show how the velocity of each electron is affected by the position of the other electron. In the calculations that follow, all results are presented in atomic units (see [10], for example), which amounts to setting $m_e = e = \hbar = 1$.

3.1 Trajectories Associated with Simplest "Textbook Approximations"

Before presenting an analysis of finite-dimensional Ritz-variational approximations to the eigenfunctions of the helium atom, it is instructive to examine the causal trajectories associated with the simplest approximations to the ground and first-excited states, because of their ubiquitous presence in standard textbooks.

3.1.1 Ground State: $\Psi(0) = 1s(1)1s(2)$

We first consider the simplest approximation to the ground state, where the wavefunction $\Psi(t)$ begins in the $1s(1)1s(2)$ configuration, i.e., both electrons are inserted into the lowest energy hydrogenic eigenstates, corresponding to $c_{11}(0) = 1$ and all other $c_{ij}(0) = 0$ in (15). In most, if not all, introductory quantum mechanics texts, the $1s(1)1s(2)$ configuration is presented as a first approximation to the helium ground state, from which the lowest nonrelativistic electronic energy of the atom is estimated.

The energy of this state is the well-known first-order perturbation theory result [10],

$$\begin{aligned} E &= \langle 1s(1)1s(2)|\hat{H}^{(0)} + \hat{H}^{(1)}|1s(1)1s(2)\rangle \\ &= 2\left(-\frac{Z}{2}\right) + Z\frac{5}{8} \\ &= -2.75 \quad \text{a.u.} \end{aligned} \tag{28}$$

The associated spin eigenfunction must be the antisymmetric Σ_0^0 function, for which both electron spin vectors are trivially zero. As such, there will be no contribution from the spin-dependent term of the momentum.

Because of the non-zero matrix elements $B_{ij,kl}$, (17), between the $1s(1)1s(2)$ state and other product states (see the first row of the matrix in Table 3), higher order coefficients c_{ij}, although initially zero, will become nonzero for $t > 0$. The value of $|c_{11}(t)|^2$ is observed to oscillate between the values of roughly 1 and 0.66, so that the $1s(1)1s(2)$ state provides the principal contribution to $\Psi(t)$. Much of the remainder of the wavefunction comes from the $1s(1)2s(2)$ and $1s(2)2s(1)$ states, with total squared contributions oscillating from 0 to about 0.33. As such, about 99.7% of the wavefunction is composed of $1s$ and $2s$ orbitals. These orbitals are radially symmetric, hence θ- and ϕ-independent, implying that the B^i_{jk} and C^i_{jk} coefficients in (22)–(25) are zero. As a result, they contribute only to radial motion of the electronic Bohmian trajectories.

The remainder of the contribution to the wavefunction—less than 0.3%—is provided by the θ-dependent $1s(1)2p_0(2)$, $2p_0(1)1s(2)$ and $2p_0(1)2p_0(2)$ states. The result is that the two electrons, starting at positions $(r_1(0), \theta_1(0), \phi_1(0))$ and $r_2(0), \theta_2(0), \phi_2(0))$, will each execute radial oscillatory motion combined with minor oscillations in the θ direction. This motion is clearly nonclassical.

The temporal behaviour of the trajectories can still be quite complicated, as can be seen in the following simple numerical experiment. We have computed some trajectories for the case in which the electrons are initially situated quite close to each other on the x-axis. Because of the functional form of the hydrogenic eigenfunctions, trajectories that begin on the xy-plane remain on the plane. As a result, all motion takes place on the x-axis. In Fig. 1 are plotted the position functions $x_1(t)$ and $x_2(t)$ that correspond to several initial conditions $(x_1(0), x_2(0))$.

Near the nucleus, the trajectories demonstrate rather regular, seemingly periodic behaviour. As one moves outward, the trajectories become more complicated. Eventually, the trajectories once again become regular. In all of these cases, the nonclassical motion of the center of mass of the electron pair is easily visualized from the trajectories. For sufficiently large values of r, the electrons are, to a good approximation, stationary.

It is, of course, tempting to investigate the effect of varying the strength of the interelectronic repulsion term in the above experiment. Very briefly, as the strength is increased trajectories with a fixed initial pair of conditions $(x_1(0), x_2(0) = x_1 + \delta)$ become more complicated. However, this effect diminishes as we move away from the nucleus.

A more physically meaningful variation, however, would be in the nuclear charge Z. For example, when $Z = 1$ the two-electron system corresponds to the hydride ion, H^-. When $Z = 3$, we have the lithium ion Li^+. In both cases, we find that there is an inner, "oscillatory zone," near the nucleus followed by zone of more

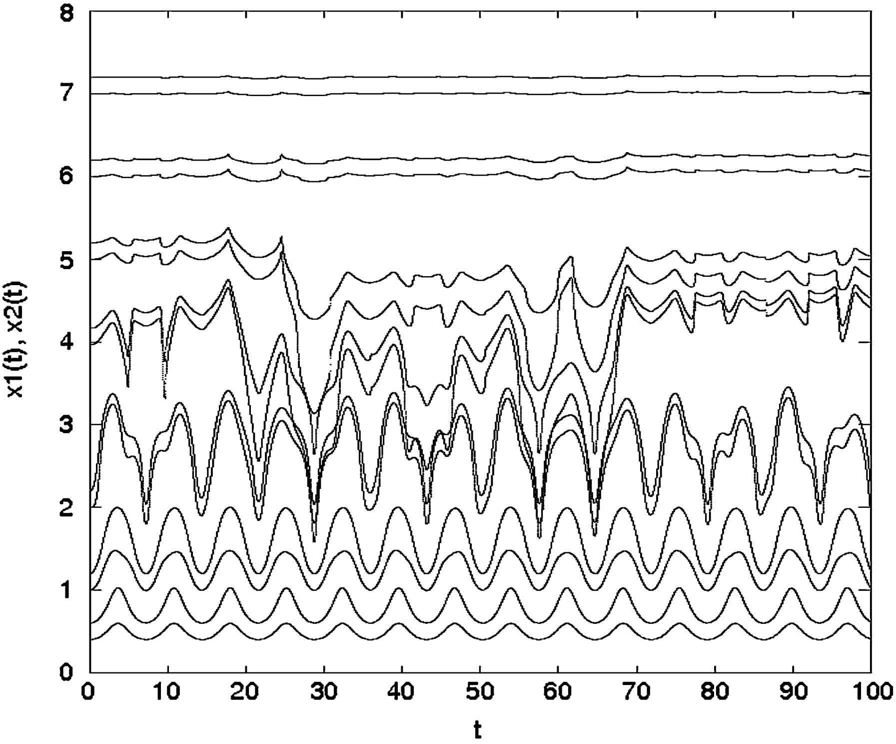

Fig. 1 Some Bohmian trajectories associated with the simplest "textbook" approximation to the helium ground state wavefunction $\Psi(t)$, where $\Psi(0) = 1s(1)1s(2)$. Electronic position functions $x_1(t)$ and $x_2(t)$ corresponding to the following initial conditions $(x_1(0), x_2(0))$: (a) (0.5, 0.7), (b) (1.0, 1.2), (c) (2.0, 2.2), (d) (4.0, 4.2), (e) (5.0, 5.2), (f) (6.0, 6.2), (g) (7.0, 7.2)

complicated trajectories, leading to a zone of "calm" sufficiently far from the nucleus. Because of the spatial and energy scaling involving Z, there are two effects of increasing (decreasing) Z: (1) the region of complicated trajectories moves toward (away from) the origin, and (2) the time scale of variations/oscillations decreases (increases).

3.1.2 Excited States

We now consider the four possible excited states—one singlet and one triplet—when one of the two electrons has been excited to the $2s$ state. These states are also presented in introductory quantum mechanics texts.

The Triplet State $\Psi(0) = \frac{1}{\sqrt{2}}[1s(1)2s(2) - 2s(1)1s(2)]$ The wavefunction $\Psi(t)$ with this initial condition has the lower of the two excited energy levels, at $E = -2.12414$ a.u. Because it is antisymmetric with respect to electron interchange, it must be associated with one of the symmetric triplet states in Table 2.

Moreover, during its time evolution, $\Psi(t)$ does not interact with any other elements of our truncated basis set. In fact, it is an eigenfunction of the 9×9 matrix representation of the Hamiltonian in our set (next section) and will be discussed in more detail below. For the moment, we simply state that the electronic motion is either stationary (Σ_0^1 spin state) or circular about the z-axis ($\Sigma_{\pm 1}^1$ spin states). (Note that this state would *not* be an eigenfunction if higher hydrogenic basis states, e.g., $3s$, were included in the set.)

The Singlet State $\Psi(0) = \frac{1}{\sqrt{2}}[1s(1)2s(2) + 2s(1)1s(2)]$ The wavefunction $\Psi(t)$ with this initial condition has a slightly higher energy at $E = -2.03635$ a.u. It must be combined with the antisymmetric singlet spin state Σ_0^0 of Table 1. As such, there is no contribution from the spin-dependent part of the momentum. The electrons will execute radial motion along with some minor θ-dependent motion, as was observed for the $1s(1)1s(2)$ case.

3.2 Eigenstates of Truncated Representation of Hamiltonian $\hat{H}$

A major motivation of this study was to examine the Bohmian trajectories of approximate eigenstates of the helium atom, with particular focus on the ground state. Here, we consider the approximations that are furnished by a classical Ritz-type variational method, namely, finite linear combinations of an appropriate set of basis functions which minimize the energy functional,

$$E(\Psi) = \langle \Psi | \hat{H} \Psi \rangle / \langle \Psi | \Psi \rangle, \tag{29}$$

where the Hamiltonian operator $\hat{H}$ is given in (10).

The finite-dimensional basis set employed in these calculations has already been described in Sect. 2. It is composed of the nine tensor product states, $\Psi_{ij}^{(0)}$, cf. (13), produced by the $1s$, $2s$ and $2p_0$ hydrogenic states, cf. (19). In this truncated basis, the Hamiltonian operator $\hat{H}$ has a 9×9 matrix representation, to be denoted as $\mathbf{H}_9$. Moreover, $\mathbf{H}_9$ is symmetric, so that its eigenvalues are real-valued.

The nine eigenvalues and eigenvectors of $\mathbf{H}_9$, which are Ritz approximations to, respectively, the true eigenvalues and eigenfunctions of the nonrelativistic helium atom, are presented in Table 2. We have labelled the eigenvalues as E_α and associated eigenfunctions as Ψ_α, $0 \le \alpha \le 8$, in ascending order of energy. For simplicity, in the discussion that follows we shall refer to the latter as simply "eigenfunctions" or "eigenstates". Because of the symmetry of the helium Hamiltonian $\hat{H}$ (and consequently, of $\mathbf{H}_9$) with respect to electron interchange, the eigenstates Ψ_α are either symmetric (S) or antisymmetric (AS) with respect to this interchange. Six states are symmetric and three states are antisymmetric.

The lowest energy eigenstate Ψ_0, a symmetric state, has energy $E_0 = -2.83181$ a.u., which has a percentage error of -2.48% compared to the best (i.e., lowest) upper bound to the nonrelativistic ground state energy of -2.90372433 a.u. [10].

We now examine the time-evolution of the eigenstates Ψ_α. First denote the expansions these eigenstates with respect to the basis elements $\Psi_{ij}^{(0)}$ as follows,

$$\Psi_\alpha = \sum_{i,j}^{3} e_{ij}^{(\alpha)} \Psi_{ij}^{(0)}. \tag{30}$$

Table 2 The expansion coefficients $e_{ij}^{(\alpha)}$, cf. (30), and energy expectation values E_α of the approximate eigenstates, Ψ_α, along with their symmetry with respect to particle interchange: "S" = symmetric, "AS" = antisymmetric

α	E_α	e_{11}	e_{12}	e_{13}	e_{21}	e_{22}	e_{23}	e_{31}	e_{32}	e_{33}	Symmetry
0	−2.83181	0.95265	−0.21431	0	−0.21431	−0.01563	0	0	0	−0.01918	S
1	−2.12414	0	−0.70711	0	0.70711	0	0	0	0	0	AS
2	−2.04994	0	0	0.70673	0	0	−0.02305	−0.70673	0.02305	0	AS
3	−1.98031	0	0	0.70709	0	0	0.00445	0.70709	0.00445	0	S
4	−1.95747	−0.30289	−0.67342	0	−0.67342	0.02984	0	0	0	−0.01934	S
5	−0.73297	0	0	0.02305	0	0	0.70673	−0.02305	−0.70673	0	AS
6	−0.72637	0.01601	0.02260	0	0.02260	0.89684	0	0	0	−0.44091	S
7	−0.61713	0	0	0.00445	0	0	−0.70709	0.00445	−0.70709	0	S
8	−0.57850	0.02171	−0.00799	0	−0.00799	0.44107	0	0	0	0.89714	S

The coefficients $e_{ij}^{(\alpha)}$ are listed in Table 2. The time-evolution of the eigenstates $\Psi_\alpha(t)$ is determined by the trivial time evolution of coefficients $c_{ij}^{(\alpha)}(t)$ of the eigenvalue expansion in (15), namely,

$$c_{ij}^{(\alpha)}(t) = e_{ij}^{(\alpha)} \exp(-iE_\alpha t/\hbar). \tag{31}$$

The real and imaginary parts of these coefficients, $a_{ij}(t)$ and $b_{ij}(t)$, respectively, are then used in (22) and (27) to drive the evolution of the trajectories.

The very simple evolution of these coefficients has, in fact, an important consequence on the Bohmian trajectories associated with the eigenstates Ψ_α. Consider (22) which describes the spin-independent contribution to the momenta of the electrons. From the behaviour of the $a_{ij}(t)$ and $b_{ij}(t)$ coefficients, each term in the summation in (22) is zero. In other words,

$$\nabla_i S_\alpha = 0, \quad i = 1, 2, \text{ for all eigenstates } \Psi_\alpha, \ 0 \le \alpha \le 8. \tag{32}$$

(Note that this result is quite analogous to that for $m = 0$ eigenstates of the hydrogen atom [4].) As a result, any motion of the electrons for eigenstates is due only to the spin-dependent momentum term in (20), which we now investigate.

In order that the total wavefunction be antisymmetric with respect to electron interchange, the six spatially-symmetric states, i.e., $\alpha \in \{0, 3, 4, 6, 7, 8\}$, must be multiplied by the antisymmetric singlet spin function Σ_0^0 in Table 1. In this case, both spin vectors $\mathbf{s}_i$ are zero, so that the spin-dependent momentum is zero. Therefore,

> *Both electrons are stationary when the helium atom is in any of the spatially-symmetric eigenstates given in Table 2. This includes the lowest energy eigenstate,* $\Psi_0(t)$.

When the system is in one of the spatially-antisymmetric eigenstates, i.e., $\alpha \in \{1, 2, 5\}$, it must be multiplied by one of the symmetric triplet spin functions in Table 1. There will be no motion for the Σ_0^1 spin state because both spin vectors $\mathbf{s}_i$ are zero. We now consider the nonzero $\Sigma_{\pm 1}^0$ spin states.

Since the spatial basis functions involve only products of the three hydrogenic eigenfunctions $1s$, $2s$ and $2p_0$, $\Psi_\alpha(t)$ does not depend upon the azimuthal coordinates ϕ_i of the electrons. As such, the terms $\nabla_i \rho$ have non-zero components only in the radial (r) and polar (θ) directions for $i = 1, 2$, i.e.,

$$\nabla_i \rho = P_i \hat{\mathbf{e}}_r + Q_i \hat{\mathbf{e}}_\theta, \tag{33}$$

where $P_i = P_i(r_1, \theta_1, r_2, \theta_2)$ and $Q_i = Q_i(r_1, \theta_1, r_2, \theta_2)$ are functions whose specific form is not important for this discussion. Taking the cross product of $\nabla_i \rho$ and $\mathbf{s}_i$ yields the following result for the spin-dependent momentum terms:

$$\frac{1}{\rho} \nabla_i \rho \times \mathbf{s}_i = -\frac{1}{\rho} [P_i \sin\theta + Q_i \cos\theta] \hat{\mathbf{e}}_\phi, \quad i = 1, 2. \tag{34}$$

Recall that these terms will account for all of the electronic momenta $\mathbf{p}_i$. Since these momenta are orthogonal to the spin vectors, $\mathbf{s}_i$, it follows that the z-coordinates,

$z_i = r_i \cos\theta_i$, are constant. And since the motion is only in the ϕ_i directions, it follows that r_i and θ_i are constant. Consequently, *the electronic trajectories are circles parallel to the xy-plane and centered around the z-axis*.

The angular velocity of each electron is given by

$$\frac{d\phi_i}{dt} = \frac{p_{i\phi}}{mr_i \sin\theta_i}, \tag{35}$$

where $p_{i\phi}$ denotes the ϕ-component of $\mathbf{p}_i$. Since r_i and θ_i are constant, the functions P_i, Q_i and $R^2 = \rho$ in (34) are constant. In other words, the *angular velocity* of each electron is constant in time. The actual value of the velocity will depend upon the initial condition of each electron.

A similar result follows for the "spin down" state Σ^1_{-1}. In this case, the direction of electronic motion is simply reversed because (i) the directions of the spin vectors $\mathbf{s}_i$ are flipped and (ii) there is no contribution from the spin-independent term due to the fact that $\nabla_i S_\alpha = 0$ for the eigenstates.

Finally, all of the above results have been verified by means of numerical computations.

4 Discussion and Concluding Remarks

In this paper, we have examined the de Broglie-Bohm deterministic trajectories for the two electrons in the helium atom. Some simple approximations to the wavefunction were provided by a low-dimensional set of basis functions constructed by means of tensor products of hydrogenic eigenfunctions. Our examination was limited to eigenfunctions with zero angular quantum number m, since we were primarily interested in trajectories associated with the ground state.

For all eigenstates, it was shown that $\nabla_i S_\alpha = 0$, implying that any electronic motion would be due to the spin-dependent part of the guidance equation. The spatial parts of six eigenstates, which includes the ground state, are symmetric with respect to electron interchange. This implies that they must be combined with the singlet spin state, Σ^0_0, for which both electronic spin vectors $\mathbf{s}_i$ are zero. As a result, both electrons are stationary when in any of these states.

The three remaining eigenstates are spatially antisymmetric and must be combined with one of the three triplet spin states $\Sigma^1_{S_z}$, $S_z \in \{-1, 0, 1\}$. For $S_z = 0$, the electrons are once again stationary. For $S_z = \pm 1$, the two electrons will move on planes of constant z-value, executing circular orbits around the z-axis with constant angular velocity.

Perhaps the most important conclusion of this paper is that the equations

$$\nabla_i S_\alpha(\mathbf{r}_1, \mathbf{r}_2, t) = 0, \quad i = 1, 2, \tag{36}$$

hold for all approximate eigenstates Ψ_α obtained by the diagonalization of the helium atom Hamiltonian in a finite basis set composed of tensor product functions $\Psi^{(0)}_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ in (13), *independent of the size of the basis set*. In other words, *the accuracy/inaccuracy associated with the truncation of the infinite-dimensional basis is irrelevant as far as the qualitative behaviour of the causal trajectories of the eigenstates is concerned.*

This conclusion follows from

1. the symmetry of the factor involving expansion coefficients a_{ij} and b_{ij} in (22) and
2. their time evolution, in particular, the fact that all coefficients associated with a given eigenfunction $\Psi_\alpha(t)$ oscillate at a common frequency, $\omega_\alpha = E_\alpha/\hbar$.

As such, all electronic motion is due to the spin-dependent momentum term, $\rho^{-1}\nabla_i \rho \times \mathbf{s}_i$. That being said, the motion produced by this term is quite specialized due to the restricted nature of the spin vectors $\mathbf{s}_i$ associated with two-spin eigenfunctions. Either the electrons are stationary, or they orbit about the z-axis, which is assumed to be aligned with the spin axes.

Regarding the ground state approximation $\Psi_0(t)$, the addition of more hydrogenic eigenfunctions to the basis set—even states with nonzero m quantum number—will decrease the energy E_0 (it is an upper bound to the true ground-state energy of the helium atom) but will not affect the associated Bohmian trajectories. Since $\Psi_0(t)$ is symmetric with respect to particle interchange, it must be combined with the antisymmetric singlet spin state Σ_0^0, for which the spin vectors are zero. As such, both electrons will be stationary, in any approximation. The same can be said for the other spatially-symmetric eigenstates $\Psi_\alpha(t)$ that must be combined with the Σ_0^0 spin state.

If hydrogenic eigenfunctions ψ_{nlm} of higher l and m values are added to the basis set, then some interesting trajectories might be produced for spatially-antisymmetric eigenstates Ψ_α that are combined with the Σ_{-1}^1 and Σ_1^1 spin-states, for which the electronic spin vectors $\mathbf{s}_i$ are nonzero.

It may be possible to produce nontrivial Bohmian trajectories by means of linear combinations of the eigenstates $\Psi_\alpha(t)$, as was observed for hydrogen [4]. Such a linear combination would have to be coupled with an appropriate spin state. (This implies that the eigenstates being combined would have to possess the same spatial symmetry.) We have already seen an example: the simple textbook approximation to the hydrogenic ground state, $1s(1)1s(2)\Sigma_0^0(1,2)$, studied earlier. As expected, this wavefunction may be expressed as a linear combination of the spatially symmetric eigenstates of $\mathbf{H}_9$:

$$1s(1)1s(2) = \Psi_{11}^{(0)}(\mathbf{r}_1,\mathbf{r}_2) \approx 0.95265\Psi_0 - 0.30289\Psi_4 + 0.01601\Psi_6 + 0.02170\Psi_8. \tag{37}$$

As discussed earlier, its time evolution $\Psi(t)$ produces nontrivial causal trajectories that demonstrate oscillatory behaviour in the r and θ coordinates, while ϕ is constant.

We conclude this paper with a comment on the suitability of the eigenfunction expansion approach adopted in this paper, in which a basis comprised of tensor products of one-particle hydrogenic atom wavefunctions was used. Of course, the basis set is perfectly tailored for the unperturbed Hamiltonian $H^{(0)}$. Moreover, the computation of the matrix elements of the interelectronic repulsion term is straightforward. In this way, the time-dependent partial differential equation for the wavefunction $\Psi(\mathbf{r}_1,\mathbf{r}_2,t)$ is reduced to a system of first-order differential equations in the time-dependent (complex) expansion coefficients $c_{ij}(t)$. The eigenfunction expansion approach also permits an analysis of the qualitative behaviour of causal trajectories

Table 3 Matrix elements, $B_{ij,kl}$, up to the constant factor $\frac{Ze^2}{a_0}$

$(i,j)\backslash(k,l)$	(1, 1)	(1, 2)	(1, 3)	(2, 1)	(2, 2)	(2, 3)	(3, 1)	(3, 2)	(3, 3)
(1, 1)	$\frac{5}{8}$	$\frac{4096\sqrt{2}}{64827}$	0	$\frac{4096\sqrt{2}}{64827}$	$\frac{16}{729}$	0	0	0	$\frac{112}{6561}$
(1, 2)	$\frac{4096\sqrt{2}}{64827}$	$\frac{17}{81}$	0	$\frac{16}{729}$	$\frac{512\sqrt{2}}{84375}$	0	0	0	$-\frac{256\sqrt{2}}{28125}$
(1, 3)	0	0	$\frac{59}{243}$	0	0	$\frac{512\sqrt{2}}{84375}$	$\frac{112}{6561}$	$-\frac{256\sqrt{2}}{28125}$	0
(2, 1)	$\frac{4096\sqrt{2}}{64827}$	$\frac{16}{729}$	0	$\frac{17}{81}$	$\frac{512\sqrt{2}}{84375}$	0	0	0	$-\frac{256\sqrt{2}}{28125}$
(2, 2)	$\frac{16}{729}$	$\frac{512\sqrt{2}}{84375}$	0	$\frac{512\sqrt{2}}{84375}$	$\frac{77}{512}$	0	0	0	$\frac{15}{512}$
(2, 3)	0	0	$\frac{512\sqrt{2}}{84375}$	0	0	$\frac{83}{512}$	$-\frac{256\sqrt{2}}{28125}$	$\frac{15}{512}$	0
(3, 1)	0	0	$\frac{112}{6561}$	0	0	$-\frac{256\sqrt{2}}{28125}$	$\frac{59}{243}$	$\frac{512\sqrt{2}}{84375}$	0
(3, 2)	0	0	$-\frac{256\sqrt{2}}{28125}$	0	0	$\frac{15}{512}$	$\frac{512\sqrt{2}}{84375}$	$\frac{83}{512}$	0
(3, 3)	$\frac{112}{6561}$	$-\frac{256\sqrt{2}}{28125}$	0	$-\frac{256\sqrt{2}}{28125}$	$\frac{15}{512}$	0	0	0	$\frac{501}{2560}$

that would not have been possible with mesh-based numerical methods, e.g. finite-element, finite-difference schemes. That being said, we have not investigated the use of other basis sets, e.g., Gaussians, plane waves and therefore cannot comment on their utility.

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Appendix: Matrix Elements of the $\frac{e^2}{r_{12}}$ Operator

In Table 3 are presented, up to the constant factor $\frac{Ze^2}{a_0}$, the matrix elements $B_{ij,kl}$ of the electronic repulsion operator for the 9-dimensional basis set of functions

$$\Psi_{ij}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{n_i,l_i,m_i}(\mathbf{r}_1)\psi_{n_j,l_j,m_j}(\mathbf{r}_2), \quad 1 \le i, j \le 3, \tag{38}$$

used in this paper. In atomic units, they must be multiplied by the factor Z.

The matrix element $B_{1,1,1,1}$ represents the well-known first-order perturbation correction to the energy for the $1s(1)1s(2)$ configuration.

These matrix elements were computed using the MAPLE computer algebra language, using the standard expansion of the $1/r_{12}$ in terms of spherical harmonics.

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