Exact norm-conserving stochastic time-dependent Hartree–Fock

2005 J. Phys. A: Math. Gen. 38 943

(http://iopscience.iop.org/0305-4470/38/4/013)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **38** (2005) 943–956 doi:10.1088/0305-4470/38/4/013

Exact norm-conserving stochastic time-dependent Hartree–Fock

Luca Tessieri[1], **Joshua Wilkie**[2] **and Murat Çetinbaş**[2]

[1] Instituto de Física y Matemáticas, Universidad Michoacana de San Nicolás de Hidalgo 58060, Morelia, Michoacán, Mexico
[2] Department of Chemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada

Received 20 May 2004
Published 12 January 2005
Online at stacks.iop.org/JPhysA/38/943

Abstract
We derive an exact single-body decomposition of the time-dependent Schrödinger equation for N pairwise interacting fermions. Each fermion obeys a stochastic time-dependent norm-preserving wave equation. As a first test of the method, we calculate the low energy spectrum of helium. An extension of the method to bosons is outlined.

PACS numbers: 03.65.−w, 02.50.−r, 02.70.−c

1. Introduction

Solution of the Schrödinger equation for pairwise interacting identical fermions is a difficult computational problem with applications in many areas of chemistry and physics. The development of accurate and computationally efficient schemes for calculating the ground and excited electronic states of molecules is a longstanding goal of theoretical chemistry [1]. Electron dynamics plays an important role in molecular electronics [2] and atomic and molecular dynamics in strong time-varying external fields [1]. The N-body problem for fermions also arises in shell models in nuclear physics [3]. Exact strategies for N-body problems generally have computational costs which scale exponentially with the number of particles. Here we show that exact solutions of the N-fermion time-dependent Schrödinger equation can be obtained via a multi-configuration Hartree–Fock Ansatz in which the single-particle wavefunctions for each configuration obey norm-conserving stochastic wave equations. Since all properties of the N-fermion problem can be calculated from the exact time-evolving wavefunction, and since the computational costs appear to scale favourably with the number of electrons, this method could provide a useful alternative to other computational strategies such as time-dependent density-functional theory [1] and auxiliary-field quantum Monte Carlo [3].

The technique of decomposing high-dimensional deterministic equations into lower dimensional stochastic wave equations was pioneered by Gisin and Percival [4] who were

able to reduce deterministic master equations for the density matrix into stochastic equations for a wavefunction. More recently the same approach was used to reduce the N-boson Liouville equation into one-boson stochastic wave equations [5]. Similar decompositions have been obtained for fermions [6] and vibrations [7]. Unfortunately, the norms of the single-particle stochastic wavefunctions grow exponentially for the boson and fermion decompositions [5, 6]. This is the wave equation analogue of the 'sign problem' which plagues path integral Monte Carlo approaches [3, 8]. The decomposition for vibrations was derived using a stochastic generalization of the time-dependent McLachlan variational principle [7], and as a consequence the equations conserve norm. Here we derive a similar norm conserving decomposition for fermions. We demonstrate the use of the method by computing the low energy spectrum of helium. Finally, we explain how the same approach can be applied to bosons.

Before outlining the derivation in section 3, we summarize the method here for readers who may not be interested in details. In section 4, we explicitly prove that the method is exact and that the single-body wave equations are norm conserving. Section 5 discusses an application of the method to helium. In section 6 we explain how the method can be adapted for identical bosons.

We consider the general N *identical* particle time-independent Hamiltonian

$$\mathcal{H}_N = \sum_{i=1}^{N} H(i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V(i, j), \tag{1}$$

where $H(i)$ denotes the single-body Hamiltonian instantiated for particle i. For electrons in molecules $H = -\hbar^2\nabla^2/2m_e - \sum_{k=1}^{M} Z_k e^2/|\mathbf{r} - \mathbf{R}_k|$, for example, where the sum is over the nuclei of the molecule. The pairwise interaction $V(i, j)$ between particles i and j is represented via

$$V(i, j) = \sum_{s=1}^{p} \hbar\omega_s O_s(i) O_s(j) \tag{2}$$

as a sum of products of dimensionless one-body (Hermitian or anti-Hermitian) operators O_s. In section 2 we prove that such an expansion is always possible. The coefficients $\hbar\omega_s$ have units of energy and may be positive or negative. This expansion is developed for the Coulomb interaction $e^2/|\mathbf{r}_i - \mathbf{r}_j|$ in section 5 (see also the appendix). Extension of the method outlined here to time-dependent Hamiltonians is straightforward: simply replace H and O_s by their time-dependent analogues in (5).

A general initial N-fermion wavefunction can be written as a weighted sum of Slater determinants of N single-particle wavefunctions. For our purposes, the single-particle wavefunctions for a given determinant should be chosen so that they are linearly independent and normalized but non-orthogonal. Each Slater determinant can then be evolved independently. For simplicity we now confine our attention to one such initial state

$$|\Psi(0)\rangle = \beta A|\phi_1(0)\rangle|\phi_2(0)\rangle \cdots |\phi_N(0)\rangle, \tag{3}$$

where A is the anti-symmetrization operator [9] and β is a normalization constant. Here the position of a 'ket' in the product indicates which electron it refers to, i.e., for $|\phi_1\rangle|\phi_2\rangle$ electron 1 is in state $|\phi_1\rangle$ and electron 2 is in state $|\phi_2\rangle$ while for $|\phi_2\rangle|\phi_1\rangle$ electron 1 is in state $|\phi_2\rangle$ and electron 2 is in state $|\phi_1\rangle$. This convention allows us to express some equations more simply than would otherwise be possible.

In our method the exact state $|\Psi(t)\rangle$ evolved from (3) is constructed from the solutions $|\phi_j(t)\rangle$ of time-dependent stochastic wave equations. Specifically, the exact N-fermion

wavefunction is expressed in terms of an average $M[\cdots]$ via

$$|\Psi(t)\rangle = \beta M[A|\phi_1(t)\rangle|\phi_2(t)\rangle\cdots|\phi_N(t)\rangle] \tag{4}$$

where the $|\phi_j(t)\rangle$ obey Itô-type [10] stochastic equations

$$\begin{aligned} \mathrm{d}|\phi_j\rangle = {} & \left(-\frac{\mathrm{i}}{\hbar}H|\phi_j\rangle + \frac{\mathrm{i}}{2}\sum_{k\neq j}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_j\langle O_s\rangle_k|\phi_j\rangle - \mathrm{i}\sum_{k\neq j}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_k O_s|\phi_j\rangle\right)\mathrm{d}t \\ & + \sum_{s=1}^{p}\sqrt{-\mathrm{i}\omega_s}(O_s - \langle O_s\rangle_j)|\phi_j\rangle\,\mathrm{d}W_s \\ & - \sum_{k\neq j}\sum_{s=1}^{p}|\omega_s|\langle\phi_j|\phi_j\rangle\frac{\langle O_s^\dagger O_s\rangle_j - |\langle O_s\rangle_j|^2}{2(N-1)\,\mathrm{Re}\{\langle\phi_j|\phi_k\rangle\}}|\phi_k\rangle\,\mathrm{d}t \end{aligned} \tag{5}$$

for $j = 1, \ldots, N$. Here we use a notation where $\langle F\rangle_j = \langle\phi_j|F|\phi_j\rangle/\langle\phi_j|\phi_j\rangle$ for any single-body operator F. For notational simplicity, the explicit time dependence of $|\phi_j\rangle$ and of the stochastic random variables $\mathrm{d}W_s$ has not been indicated. (Note that in the case of electrons $|\phi_j\rangle$ are similar to the spin-orbit single-particle wavefunctions of Hartree–Fock.) The symbols $\mathrm{d}W_s(t)$ represent independent normally distributed real stochastic differentials with

$$M[\mathrm{d}W_s(t)] = 0 \qquad \text{and} \qquad M[\mathrm{d}W_r(t)\,\mathrm{d}W_s(t)] = \delta_{rs}\,\mathrm{d}t. \tag{6}$$

The second condition imposes statistical independence of the stochastic differentials.

Imagine a sequence of time steps all of equal length $\mathrm{d}t$ such that $t = m\,\mathrm{d}t$ for some integer m. At each time step a set of stochastic differentials is sampled from the normal distribution

$$P(\mathrm{d}\mathbf{W}(l\,\mathrm{d}t)) = [1/(2\pi\,\mathrm{d}t)]^{p/2}\exp\{-\mathrm{d}\mathbf{W}(l\,\mathrm{d}t)\cdot\mathrm{d}\mathbf{W}(l\,\mathrm{d}t)/2\,\mathrm{d}t\},$$

where $\mathrm{d}\mathbf{W}(l\,\mathrm{d}t) = (\mathrm{d}W_1(l\,\mathrm{d}t), \ldots, \mathrm{d}W_p(l\,\mathrm{d}t))$ is the vector of stochastic differentials (p is the number of components of $\mathrm{d}\mathbf{W}$). Note that l runs from 1 to m. The expectation (4) at any time t can thus be represented in the form

$$|\Psi(t)\rangle = \beta\prod_{l=1}^{m}\int \mathrm{d}^p W(l\,\mathrm{d}t)P(\mathrm{d}\mathbf{W}(l\,\mathrm{d}t))A|\phi_1(t)\rangle|\phi_2(t)\rangle\cdots|\phi_N(t)\rangle$$

and Monte Carlo sampling of the integrals then yields the stochastic paths generated by equations (5). Each time sequence of sampled stochastic differentials defines one set of stochastic variables $W_s(t)$ (i.e., Wiener process). Each realization of the set of stochastic variables $W_s(t)$ as a function of time thus yields one Slater determinant in the average $M[\cdots]$. Since single-particle norms are conserved, each Slater determinant is equally weighted in the average, and error in the mean will scale as $1/\sqrt{L}$ where L is the number of realizations.

The single-particle wavefunctions on the right-hand side of (5) are independent of the stochastic differentials $\mathrm{d}W_s(t)$ and so averages such as $M[F(\phi_1(t), \ldots, \phi_N(t))g(\mathrm{d}W_1(t), \ldots, \mathrm{d}W_p(t))]$ can be calculated via the simplified formula $M[F(\phi_1(t), \ldots, \phi_N(t))]M[g(\mathrm{d}W_1(t), \ldots, \mathrm{d}W_p(t))]$. This fact is implicit in proofs of norm conservation and exactness outlined in section 4.

The fact that all matrix elements (e.g. $\langle\phi_j|O_s|\phi_j\rangle$) in the stochastic equations involve single-particle operators, and the sum over index $k \neq j$ for each $|\phi_j\rangle$, show that the computational costs will scale at least quadratically with the number of electrons. For implementations similar to that for He, discussed in section 5, the number of terms in the two-body expansion *in principle* scales as the square of the number of electrons (in practice many $\hbar\omega_s$ may be small or zero which could improve the scaling of the method), and hence evaluation of all $\langle\phi_j|O_s|\phi_j\rangle$ for each j requires N^4 operations, making the method scale as

$O(N^5)$ overall. The precise scaling is obviously model dependent but computational costs should be somewhere in the range $O(N^2)$ to $O(N^5)$. Most alternative exact approaches have computational costs which scale exponentially with the number of electrons.

The most important properties of the stochastic decompositions (4) and (5) are its exactness and its norm conservation.

Equations (5) conserve norm in the mean (i.e., $M[\langle\phi_j(t)|\phi_j(t)\rangle] = 1$) which gives our decomposition distinct numerical advantages over other decompositions in which the mean norm grows exponentially [6]. In addition, our method conserves norm exactly for each individual stochastic realization (see section 4). Note that the norm of $A|\phi_1(t)\rangle$ $|\phi_2(t)\rangle \ldots |\phi_N(t)\rangle$ is *not* conserved by our method because the single-particle states are non-orthogonal. This however presents no problem numerically.

Using the Itô calculus [10] we also show in section 5 that

$$\begin{aligned} \mathrm{d}|\Psi(t)\rangle = \beta M \Bigg[& \sum_{j=1}^{N} A|\phi_1(t)\rangle \cdots |\,\mathrm{d}\phi_j(t)\rangle \cdots |\phi_N(t)\rangle \\ & + \sum_{j=1}^{N-1} \sum_{k=j+1}^{N} A|\phi_1(t)\rangle \cdots |d\phi_j(t)\rangle \cdots |\,\mathrm{d}\phi_k(t)\rangle \cdots |\phi_N(t)\rangle \Bigg] \\ = & -\frac{\mathrm{i}}{\hbar}\mathcal{H}_N|\Psi(t)\rangle\,\mathrm{d}t \end{aligned} \tag{7}$$

which implies that the method is exact for all forms of our equations.

Explicit time dependence of the N-fermion wavefunction is of direct interest in many chemical problems. Energies can be extracted via the Fourier transform of the time auto-correlation function $\langle\Psi(0)|\Psi(t)\rangle$. In practice, one computes the function

$$I(E) = \frac{1}{\pi\hbar}\mathrm{Re}\int_0^T \langle\Psi(0)|\Psi(t)\rangle \exp\left(\frac{\mathrm{i}Et}{\hbar}\right)\mathrm{d}t \simeq \langle\Psi(0)|\delta(E-\mathcal{H}_N)|\Psi(0)\rangle \tag{8}$$

which will have maxima at the true energies when the end point of integration T is sufficiently large. The method therefore also provides access to spectral information and in fact it is straightforward to generalize (8) so that states of specific parity can be extracted. Eigenfunctions can also be obtained.

2. Single-body decomposition of pairwise interaction

Consider a general two-body interaction $V(1,2)$. We will now show that it can be expanded in products of one-body interactions according to equation (2). Let $|i\rangle$ with $i = 1, 2, \ldots$ denote a complete basis of the one-body space. Then $|i_1; i_2\rangle = |i_1\rangle|i_2\rangle$ for $i_1, i_2 = 1, 2, \ldots$ will be a complete basis of the two-body space. Here again we employ the convention that the position of a 'ket' in a product identifies the fermion. It follows then that we may represent the interaction via

$$V(1,2) = \sum_{i_1=1}^{\infty}\sum_{i_2=1}^{\infty}\sum_{j_1=1}^{\infty}\sum_{j_2=1}^{\infty}|i_1; i_2\rangle\langle i_1; i_2|V(1,2)|j_1; j_2\rangle\langle j_1; j_2|, \tag{9}$$

where we have inserted closure relations for the two-body space on either side.

Define a bijective application $\sigma : \mathbf{N}^2 \to \mathbf{N}$ which maps each couple of integers (i, j) in a unique integer $\sigma(i, j)$. Then we can introduce new composite indices $\sigma_1 = \sigma(i_1, j_1)$ for body 1 and $\sigma_2 = \sigma(i_2, j_2)$ for body 2 with σ_1 and σ_2 taking integer values $1, 2, \ldots$. We may then define matrix elements

$$\mathcal{V}_{\sigma_1,\sigma_2} = \langle i_1; i_2|V(1,2)|j_1; j_2\rangle$$

which are symmetric under the interchange of σ_1 and σ_2. This symmetry reflects the indistinguishability of the particles. Diagonalizing $\mathcal{V}$ then gives

$$\mathcal{V}_{\sigma_1,\sigma_2} = \sum_{s=1}^{\infty} \hbar\omega_s Q_{\sigma_1,s} Q_{\sigma_2,s}, \tag{10}$$

where $\hbar\omega_s$ are the eigenvalues and $Q_{\sigma,s}$ are the dimensionless matrix elements of the orthogonal transformation. With a slight change of notation and using the inverse of the mapping $\sigma_1 = \sigma(i_1, j_1)$ we may then write

$$Q_{\sigma_1,s} = \langle i_1|O_s|j_1\rangle \tag{11}$$

which defines the one-body operator O_s. Since $V(1, 2)$ is Hermitian it follows that each O_s must be either Hermitian or anti-Hermitian. The eigenvalues $\hbar\omega_s$ may be positive or negative.

Substituting (11) into (10), and (10) into (9) gives

$$\begin{aligned} V(1,2) &= \sum_{i_1=1}^{\infty}\sum_{i_2=1}^{\infty}\sum_{j_1=1}^{\infty}\sum_{j_2=1}^{\infty} |i_1; i_2\rangle \sum_{s=1}^{\infty} \hbar\omega_s \langle i_1|O_s|j_1\rangle\langle i_2|O_s|j_2\rangle \langle j_1; j_2| \\ &= \sum_{s=1}^{\infty} \hbar\omega_s \sum_{i_1=1}^{\infty}\sum_{i_2=1}^{\infty}\sum_{j_1=1}^{\infty}\sum_{j_2=1}^{\infty} |i_1; i_2\rangle\langle i_1; i_2|O_s(1)O_s(2)|j_1; j_2\rangle\langle j_1; j_2|. \end{aligned}$$

Finally removing the closure relations gives

$$V(1,2) = \sum_{s=1}^{\infty} \hbar\omega_s O_s(1) O_s(2)$$

which is the desired expansion.

In practice, a finite basis set is more practical than a complete one but the same considerations apply except that the sum will terminate at some finite value p.

3. Derivation of stochastic wave equations

We originally derived the stochastic decomposition discussed above using the stochastic McLachlan variational principle developed in [7]. Here we present a more direct argument. For simplicity we initially focus on just two fermions with the simplest possible interaction. Consider then the restricted two-fermion Hamiltonian

$$\mathcal{H}_2 = H(1) + H(2) + \hbar\omega O(1) O(2) \tag{12}$$

and a normalized initial wavefunction of the form

$$|\Psi(0)\rangle = \beta(|\phi_1(0)\rangle|\phi_2(0)\rangle - |\phi_2(0)\rangle|\phi_1(0)\rangle),$$

where $\beta = 1/\sqrt{2(1 - |\langle\phi_1(0)|\phi_2(0)\rangle|^2)}$ is a normalization factor, and $|\phi_1(0)\rangle$ and $|\phi_2(0)\rangle$ are normalized but non-orthogonal states, i.e.,

$$\langle\phi_1(0)|\phi_1(0)\rangle = \langle\phi_2(0)|\phi_2(0)\rangle = 1 \qquad \text{and} \qquad \langle\phi_1(0)|\phi_2(0)\rangle \neq 0.$$

Note the antisymmetric form of the initial wavefunction.

We wish to find stochastic equations for $|\phi_1(t)\rangle$ and $|\phi_2(t)\rangle$ such that the exact solution $|\Psi(t)\rangle$ of the Schrödinger equation

$$\mathrm{d}|\Psi(t)\rangle = -\frac{\mathrm{i}}{\hbar}\mathcal{H}_2|\Psi(t)\rangle\,\mathrm{d}t$$

can be written as the expectation value

$$|\Psi(t)\rangle = \beta M[|\Phi(t)\rangle] \tag{13}$$

of the antisymmetric stochastic vector

$$|\Phi(t)\rangle = |\phi_1(t)\rangle|\phi_2(t)\rangle - |\phi_2(t)\rangle|\phi_1(t)\rangle. \tag{14}$$

We will also require that the stochastic wave equations conserve norm

$$\langle\phi_1(t)|\phi_1(t)\rangle = \langle\phi_2(t)|\phi_2(t)\rangle = 1.$$

To achieve norm conservation the single fermion wavefunctions must satisfy the condition

$$\mathrm{d}(\langle\phi_i|\phi_i\rangle) = \langle\mathrm{d}\phi_i|\phi_i\rangle + \langle\phi_i|\mathrm{d}\phi_i\rangle + \langle\mathrm{d}\phi_i|\mathrm{d}\phi_i\rangle = 0 \tag{15}$$

for $i = 1, 2$. Since $\mathrm{d}|\phi_i(t)\rangle$ will have a term proportional to a change $\mathrm{d}W(t)$ in a stochastic process $W(t)$ with $M[\mathrm{d}W(t)^2] = \mathrm{d}t$ and $M[\mathrm{d}W(t)] = 0$, there will naturally be terms proportional to $\mathrm{d}W(t)^2$ (which is of order $\mathrm{d}t$) in condition (15). Hence it may prove useful to have a term proportional to $\mathrm{d}W(t)^2$ in $\mathrm{d}|\phi_i(t)\rangle$ in order to conserve norm. Our wave equations should therefore be of the form

$$\mathrm{d}|\phi_i\rangle = |v_i\rangle\,\mathrm{d}t + |u_i\rangle\,\mathrm{d}W + |w_i\rangle\,\mathrm{d}W^2, \tag{16}$$

where all quantities depend on the time t. With this form of the stochastic differential $\mathrm{d}|\phi_i\rangle$, condition (15) can be written as

$$2\mathrm{Re}\{\langle\phi_i|v_i\rangle\}\,\mathrm{d}t + 2\mathrm{Re}\{\langle\phi_i|u_i\rangle\}\,\mathrm{d}W + (2\mathrm{Re}\{\langle\phi_i|w_i\rangle\} + \langle u_i|u_i\rangle)\,\mathrm{d}W^2 = 0 \tag{17}$$

and the coefficients of $\mathrm{d}t$, $\mathrm{d}W$ and $\mathrm{d}W^2$ must independently vanish.

In order to reproduce the interaction term of Hamiltonian (12), we must have a term in $|u_i\rangle$ which is proportional to $O|\phi_i\rangle$. To make the coefficient of $\mathrm{d}W$ vanish in equation (17) it would thus be sufficient to choose

$$|u_i\rangle = \sqrt{-\mathrm{i}\omega}(O - \langle O\rangle_i)|\phi_i\rangle \tag{18}$$

eliminating one of the unknowns in equation (16). Here $\langle O\rangle_i = \langle\phi_i|O|\phi_i\rangle/\langle\phi_i|\phi_i\rangle$ where we keep the factor of $\langle\phi_i|\phi_i\rangle$ explicit even though it is unity.

To make the coefficient of $\mathrm{d}W^2$ vanish in equation (17) we can choose

$$\begin{aligned} |w_1\rangle &= -|\omega|\frac{\langle\phi_1|\phi_1\rangle[\langle O^\dagger O\rangle_1 - |\langle O\rangle_1|^2]}{2\mathrm{Re}\,\{\langle\phi_1|\phi_2\rangle\}}|\phi_2\rangle \\ |w_2\rangle &= -|\omega|\frac{\langle\phi_2|\phi_2\rangle[\langle O^\dagger O\rangle_2 - |\langle O\rangle_2|^2]}{2\mathrm{Re}\,\{\langle\phi_1|\phi_2\rangle\}}|\phi_1\rangle \end{aligned} \tag{19}$$

since the $|w_i\rangle$ terms were included precisely for this purpose. Clearly ϕ_1 and ϕ_2 must be non-orthogonal initially and a declining overlap will cause an increase of (19) for each mode thereby restoring the overlap.

Finally, we need to find $|v_i\rangle$. Clearly, there should be a term like $-(\mathrm{i}/\hbar)H|\phi_i\rangle$ to reproduce the single-particle terms of Hamiltonian (12). There could also be a term like $O|\phi_i\rangle$. So assume that $|v_i\rangle$ will take the form

$$|v_i\rangle = -(\mathrm{i}/\hbar)H|\phi_i\rangle + a_i|\phi_i\rangle + b_i\,O|\phi_i\rangle, \tag{20}$$

where a_i and b_i are unknowns. To make the coefficient of $\mathrm{d}t$ vanish in equation (17) it is necessary that $\mathrm{Re}\{a_i\} + \mathrm{Re}\{b_i\}\langle\phi_i|O|\phi_i\rangle = 0$. Hence we can probably set the real parts of a_i and b_i to zero. To determine their imaginary parts we consider the expectation of the differential of the vector (14) which, because of condition (13), must be equal to the differential of the vector $|\Psi(t)\rangle$, so that one has

$$\begin{aligned} \mathrm{d}|\Psi(t)\rangle = \beta M[&|\mathrm{d}\phi_1(t)\rangle|\phi_2(t)\rangle + |\phi_1(t)\rangle|\mathrm{d}\phi_2(t)\rangle + |\mathrm{d}\phi_1(t)\rangle|\mathrm{d}\phi_2(t)\rangle \\ &-|\mathrm{d}\phi_2(t)\rangle|\phi_1(t)\rangle - |\phi_2(t)\rangle|\mathrm{d}\phi_1(t)\rangle - |\,\mathrm{d}\phi_2(t)\rangle|\mathrm{d}\phi_1(t)\rangle]. \end{aligned} \tag{21}$$

Replacing the differential terms $\mathrm{d}|\phi_i\rangle$ on the right-hand side of the previous equation with expression (16) and making use of the results (18) and (19) as well as of ansatz (20), after some algebra one obtains

$$\begin{aligned}\mathrm{d}|\Psi(t)\rangle = \beta M[&-(\mathrm{i}/\hbar)(H(1)+H(2))|\Phi(t)\rangle\,\mathrm{d}t - \mathrm{i}\omega O(1)O(2)|\Phi(t)\rangle\,\mathrm{d}W^2\\ &+(a_1+a_2)|\Phi(t)\rangle\,\mathrm{d}t - \mathrm{i}\omega\langle O\rangle_1\langle O\rangle_2|\Phi(t)\rangle\,\mathrm{d}W^2 + \sqrt{-\mathrm{i}\omega}(O(1)+O(2)\\ &-\langle O\rangle_1-\langle O\rangle_2)|\Phi(t)\rangle\,\mathrm{d}W + (b_1\,\mathrm{d}t + \mathrm{i}\omega\langle O\rangle_2\,\mathrm{d}W^2)|O\phi_1(t)\rangle|\phi_2(t)\rangle\\ &+(b_2\,\mathrm{d}t + \mathrm{i}\omega\langle O\rangle_1\,\mathrm{d}W^2)|\phi_1(t)\rangle|O\phi_2(t)\rangle\\ &-(b_1\,\mathrm{d}t + \mathrm{i}\omega\langle O\rangle_2\,\mathrm{d}W^2)|\phi_2(t)\rangle|O\phi_1(t)\rangle\\ &-(b_2\,\mathrm{d}t + \mathrm{i}\omega\langle O\rangle_1\,\mathrm{d}W^2)|O\phi_2(t)\rangle|\phi_1(t)\rangle]. \end{aligned} \tag{22}$$

Using condition (13) and the facts that $M[\mathrm{d}W]=0$ and $M[\mathrm{d}W^2]=\mathrm{d}t$, and assigning

$$a_1 = a_2 = \frac{\mathrm{i}\omega}{2}\langle O\rangle_1\langle O\rangle_2, \qquad b_1 = -\mathrm{i}\omega\langle O\rangle_2 \qquad \text{and} \qquad b_2 = -\mathrm{i}\omega\langle O\rangle_1,$$

we then find that equation (22) reduces to $\mathrm{d}|\Psi(t)\rangle = -(\mathrm{i}/\hbar)\mathcal{H}_2|\Psi(t)\rangle\,\mathrm{d}t$ which is the exact Schrödinger equation in differential form. Hence we have found exact stochastic wave equations of the form

$$\begin{aligned}\mathrm{d}|\phi_1\rangle &= \Big(-\frac{\mathrm{i}}{\hbar}H|\phi_1\rangle - \mathrm{i}\omega\langle O\rangle_2 O|\phi_1\rangle + \frac{\mathrm{i}\omega}{2}\langle O\rangle_1\langle O\rangle_2|\phi_1\rangle\Big)\,\mathrm{d}t\\ &\quad + \sqrt{-\mathrm{i}\omega}(O-\langle O\rangle_1)|\phi_1\rangle\,\mathrm{d}W - |\omega|\frac{\langle\phi_1|\phi_1\rangle[\langle O^\dagger O\rangle_1 - |\langle O\rangle_1|^2]}{2\mathrm{Re}\{\langle\phi_1|\phi_2\rangle\}}|\phi_2\rangle\,\mathrm{d}W^2\\ \mathrm{d}|\phi_2\rangle &= \Big(-\frac{\mathrm{i}}{\hbar}H|\phi_2\rangle - \mathrm{i}\omega\langle O\rangle_1 O|\phi_2\rangle + \frac{\mathrm{i}\omega}{2}\langle O\rangle_1\langle O\rangle_2|\phi_2\rangle\Big)\,\mathrm{d}t\\ &\quad + \sqrt{-\mathrm{i}\omega}(O-\langle O\rangle_2)|\phi_2\rangle\,\mathrm{d}W - |\omega|\frac{\langle\phi_2|\phi_2\rangle[\langle O^\dagger O\rangle_2 - |\langle O\rangle_2|^2]}{2\mathrm{Re}\{\langle\phi_1|\phi_2\rangle\}}|\phi_1\rangle\,\mathrm{d}W^2 \end{aligned} \tag{23}$$

which conserve norm by construction. Since terms of order $\mathrm{d}W^3$ and higher are of no importance and since the average of $\mathrm{d}W^2$ is $\mathrm{d}t$, it is possible to make this replacement in equations (23) with no loss of accuracy or generality [10] giving

$$\begin{aligned}\mathrm{d}|\phi_1\rangle &= \Big(-\frac{\mathrm{i}}{\hbar}H|\phi_1\rangle - \mathrm{i}\omega\langle O\rangle_2 O|\phi_1\rangle + \frac{\mathrm{i}\omega}{2}\langle O\rangle_1\langle O\rangle_2|\phi_1\rangle\Big)\,\mathrm{d}t\\ &\quad + \sqrt{-\mathrm{i}\omega}(O-\langle O\rangle_1)|\phi_1\rangle\,\mathrm{d}W - |\omega|\frac{\langle\phi_1|\phi_1\rangle[\langle O^\dagger O\rangle_1 - |\langle O\rangle_1|^2]}{2\mathrm{Re}\{\langle\phi_1|\phi_2\rangle\}}|\phi_2\rangle\,\mathrm{d}t\\ \mathrm{d}|\phi_2\rangle &= \Big(-\frac{\mathrm{i}}{\hbar}H|\phi_2\rangle - \mathrm{i}\omega\langle O\rangle_1 O|\phi_2\rangle + \frac{\mathrm{i}\omega}{2}\langle O\rangle_1\langle O\rangle_2|\phi_2\rangle\Big)\,\mathrm{d}t\\ &\quad + \sqrt{-\mathrm{i}\omega}(O-\langle O\rangle_2)|\phi_2\rangle\,\mathrm{d}W - |\omega|\frac{\langle\phi_2|\phi_2\rangle\left[\langle O^\dagger O\rangle_2 - |\langle O\rangle_2|^2\right]}{2\mathrm{Re}\{\langle\phi_1|\phi_2\rangle\}}|\phi_1\rangle\,\mathrm{d}t. \end{aligned} \tag{24}$$

Generalization of (24) to the full pairwise interaction gives a special case of (4) and (5). We thus proceed directly in the next section to consideration of the N-fermion problem with full pairwise interaction.

4. Exactness and conservation of one-body norm

Consider conservation of norm first. To be norm conserving equation (5) must satisfy the constraint

$$\mathrm{d}(\langle\phi_j(t)|\phi_j(t)\rangle) = \langle\mathrm{d}\phi_j(t)|\phi_j(t)\rangle + \langle\phi_j(t)|\,\mathrm{d}\phi_j(t)\rangle + \langle\,\mathrm{d}\phi_j(t)|\mathrm{d}\phi_j(t)\rangle = 0$$

for $j = 1, \ldots, N$ or equivalently that

$$\mathrm{d}M[\langle\phi_j(t)|\phi_j(t)\rangle] = 0 \qquad \text{and} \qquad \mathrm{d}M[\langle\phi_j(t)|\phi_j(t)\rangle^2] = 0.$$

Substituting (5) in $\mathrm{d}M[\langle\phi_j(t)|\phi_j(t)\rangle]$ gives

$$M\left[\sum_{s=1}^{p}|\omega_s|\langle\phi_j|\phi_j\rangle(\langle O_s^\dagger O_s\rangle_j - |\langle O_s\rangle_j|^2)(\mathrm{d}W_s^2 - \mathrm{d}t)\right]$$

which vanishes. Similarly,

$$\begin{aligned}\mathrm{d}M[\langle\phi_j(t)|\phi_j(t)\rangle^2] = M[&2\langle\phi_j(t)|\phi_j(t)\rangle\,\mathrm{d}(\langle\phi_j(t)|\phi_j(t)\rangle)\\ &+2|\langle\phi_j(t)|\,\mathrm{d}\phi_j(t)\rangle|^2 + \langle\phi_j(t)|\,\mathrm{d}\phi_j(t)\rangle^2 + \langle\,\mathrm{d}\phi_j(t)|\phi_j(t)\rangle^2]\end{aligned}$$

which then gives

$$M\left[2\sum_{s=1}^{p}|\omega_s|\langle\phi_j|\phi_j\rangle^2\left(\left\langle O_s^\dagger O_s\right\rangle_j - |\langle O_s\rangle_j|^2\right)\left(\mathrm{d}W_s^2 - \mathrm{d}t\right) + O(\mathrm{d}t^2)\right]$$

which vanishes as $\mathrm{d}t \to 0$. Hence norm is exactly conserved for individual stochastic realizations as well as in the mean.

Now consider the issue of exactness of the decomposition. Substituting (5) into equation (7) we see that the term of (5) proportional to $|\omega_s|$ makes no contribution because the Slater determinants have two identical single-particle orbitals and hence vanish. The term of (5) proportional to $\mathrm{d}W_s$ makes no contribution to the first term of (7) because $M[\mathrm{d}W_s] = 0$. The first three terms of (5) contribute

$$\begin{aligned}M\Bigg[&-\frac{\mathrm{i}}{\hbar}\sum_{j=1}^{N-1}A|\phi_1\rangle\cdots|H\phi_j\rangle\cdots|\phi_N\rangle + \mathrm{i}\sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_j\langle O_s\rangle_k A|\phi_1\rangle\cdots|\phi_N\rangle\\ &-\mathrm{i}\sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_j A|\phi_1\rangle\cdots|O_s\phi_k\rangle\cdots|\phi_N\rangle\\ &-\mathrm{i}\sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_k A|\phi_1\rangle\cdots|O_s\phi_j\rangle\cdots|\phi_N\rangle\Bigg]\mathrm{d}t\end{aligned} \tag{25}$$

to the first term of (7). The non-vanishing contributions of the second term in equation (7) are

$$\begin{aligned}M\Bigg[&-\mathrm{i}\sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\sum_{s=1}^{p}\omega_s A|\phi_1\rangle\ldots|O_s\phi_j\rangle\cdots|O_s\phi_k\rangle\cdots|\phi_N\rangle\\ &-\mathrm{i}\sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_j\langle O_s\rangle_k A|\phi_1\rangle\cdots|\phi_N\rangle\\ &+\mathrm{i}\sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_j A|\phi_1\rangle\cdots|O_s\phi_k\rangle\cdots|\phi_N\rangle\\ &+\mathrm{i}\sum_{j=1}^{N-1}\sum_{k=j+1}^{N}\sum_{s=1}^{p}\omega_s\langle O_s\rangle_k A|\phi_1\rangle\cdots|O_s\phi_j\rangle\cdots|\phi_N\rangle\Bigg]\mathrm{d}t.\end{aligned} \tag{26}$$

The first terms of (25) and (26) combine to give $-(\mathrm{i}/\hbar)\mathcal{H}_N|\Psi(t)\rangle\,\mathrm{d}t$. The second terms of (25) and (26) cancel as do the third and fourth terms of the respective equations. These considerations thus show that $\mathrm{d}|\Psi(t)\rangle = -(\mathrm{i}/\hbar)\mathcal{H}_N|\Psi(t)\rangle\,\mathrm{d}t$ and hence that the method is exact.

5. Application to He

Here we apply equations (4) and (5) to the problem of calculating the low energy spectrum of helium as a first test of the method. Clearly we need a basis to represent the single electron wavefunctions. We also need a decomposition of form (2) for the Coulomb interaction.

We choose to represent the single-particle wavefunctions in a finite basis of states $|n, l, m, \tau\rangle = |\psi_{n,l,m}\rangle \otimes |\tau\rangle$ where $\psi_{n,l,m}$ are the exact orbital eigenfunctions of the He^+ ion and $|\tau\rangle = |\pm\rangle$ for $\tau = \pm$ are the spin-1/2 eigenstates. Here $n = 1, 2, \ldots, l = 0, \ldots, n-1$, and $m = -l, \ldots, 0, \ldots l$ are the allowed values of the quantum numbers. That is, the orbital parts of these basis functions are exact eigenfunctions of the single-body Hamiltonian $-\hbar^2\nabla^2/2m_e - 2e^2/r$ with eigenvalues $E_n = -2/n^2$ in atomic units (i.e. $\hbar = 1, m_e = 1$, and $e = 1$). The functional forms in the coordinate representation are

$$\langle \mathbf{r}|\psi_{n,l,m}\rangle = R_{n,l}(r)Y_{l,m}(\theta, \phi), \tag{27}$$

where $Y_{l,m}(\theta, \phi)$ are the usual spherical harmonics (i.e., eigenstates of angular momentum) and the radial functions $R_{n,l}(r)$ are

$$R_{n,l}(r) = \frac{4}{n^2}\sqrt{2\frac{(n-l-1)!}{(n+l)!}}\,\mathrm{e}^{-2r/n}\left(\frac{4r}{n}\right)^l L^{2l+1}_{n-l-1}\left(\frac{4r}{n}\right),$$

where $L^\alpha_n(x)$ are associated Laguerre polynomials defined as

$$L^\alpha_n(x) = \frac{1}{n!}\,\mathrm{e}^x x^{-\alpha}\frac{\mathrm{d}^n}{\mathrm{d}x^n}(\mathrm{e}^{-x}x^{n+\alpha}) = \sum_{k=0}^{n}(-1)^k\binom{n+\alpha}{n-k}\frac{x^k}{k!}.$$

Note that this definition of the associated Laguerre polynomials while consistent with standard mathematical usage [11] differs from those used in some standard physics texts [12].[3]

In this basis the coefficients of the single-particle wavefunctions are defined via

$$c^{(1)}_{n,l,m,\tau}(t) = \langle n, l, m, \tau|\phi_1(t)\rangle \qquad c^{(2)}_{n,l,m,\tau}(t) = \langle n, l, m, \tau|\phi_2(t)\rangle$$

and the components of the full wavefunction $\Psi(t)$ in this basis will be defined as

$$C_{n,l,m,\tau;n',l',m',\tau'}(t) = \beta M\big[c^{(1)}_{n,l,m,\tau}(t)c^{(2)}_{n',l',m',\tau'}(t) - c^{(1)}_{n',l',m',\tau'}(t)c^{(2)}_{n,l,m,\tau}(t)\big]$$

which obviously incorporate the correct antisymmetry.

The basis (27) is also used to expand the two-body interaction $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ in accord with (2). Specifically, we calculated the matrix elements

$$\langle i_1; j_1|V(1,2)|i_2; j_2\rangle = \langle\psi_{n_1,l_1,m_1}(1)\psi_{n_2,l_2,m_2}(2)|\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}|\psi_{n'_1,l'_1,m'_1}(1)\psi_{n'_2,l'_2,m'_2}(2)\rangle$$

for which we provide formulae in the appendix. Here $i_1(n_1, l_1, m_1)$, $j_1(n_2, l_2, m_2)$, $i_2(n'_1, l'_1, m'_1)$ and $j_2(n'_2, l'_2, m'_2)$ are composite integer indices ranging from 1 to infinity (or the maximum number of elements in the basis set). The procedure outlined in section 2 was then performed numerically to obtain the expansion of the two-body interaction. If due to truncation of the basis set $1 \leqslant i_1, j_1, i_2, j_2 \leqslant K$, then the number of terms in the decomposition (2) is $p = K^2$. In practice, it is convenient to consider some $n_{\max}$ from which it follows that $K = n_{\max}(n_{\max} + 1)(2n_{\max} + 1)/6$.

[3] For example, the definition $L^\alpha_n(x) = (-1)^\alpha\frac{n!}{(n-\alpha)!}\,\mathrm{e}^x x^{-\alpha}\frac{\mathrm{d}^{n-\alpha}}{\mathrm{d}x^{n-\alpha}}(e^x x^n)$ is employed in [12].

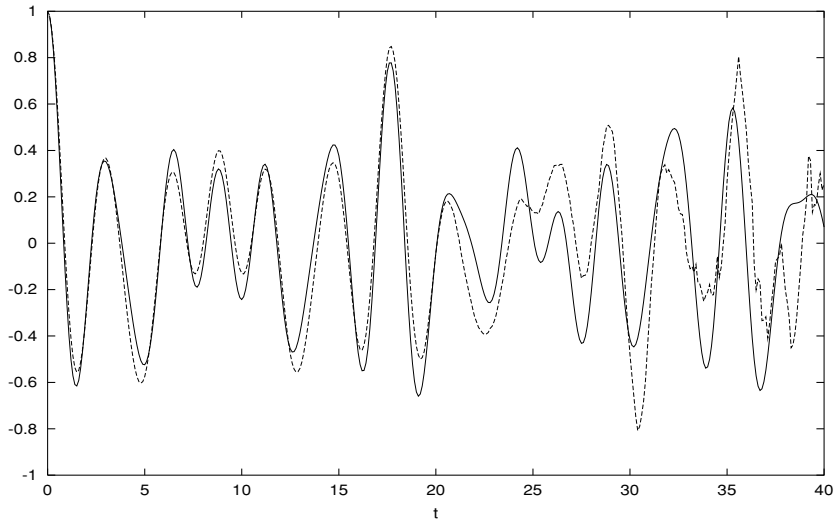

Figure 1. Re $\langle\Psi(0)|\Psi(t)\rangle$ versus t.

The stochastic equations for the coefficients thus take the form

$$\begin{aligned}
\mathrm{d}c^{(1)}_{n,l,m,\tau}(t) &= \left(\sum_{s=1}^{p}\langle O_s\rangle_1\left[\frac{\mathrm{i}}{2}\langle O_s\rangle_2\omega_s\,\mathrm{d}t-\sqrt{-\mathrm{i}\omega_s}\,\mathrm{d}W_s(t)\right]+\frac{2\mathrm{i}}{n^2}\mathrm{d}t\right)c^{(1)}_{n,l,m,\tau}(t)\\
&\quad-\left(\sum_{s=1}^{p}[\mathrm{i}\langle O_s\rangle_2\omega_s\,\mathrm{d}t-\sqrt{-\mathrm{i}\omega_s}\,\mathrm{d}W_s(t)]\right)\sum_{n',l',m'}\langle n,l,m|O_s|n',l',m'\rangle c^{(1)}_{n',l',m',\tau}(t)\\
&\quad-\left(\sum_{s=1}^{p}|\omega_s|\frac{\langle\phi_1|\phi_1\rangle\left[\langle O_s^{\dagger}O_s\rangle_1-|\langle O_s\rangle_1|^2\right]}{2\mathrm{Re}\{\langle\phi_1|\phi_2\rangle\}}\,\mathrm{d}t\right)c^{(2)}_{n,l,m,\tau}(t)\\
\mathrm{d}c^{(2)}_{n,l,m,\tau}(t) &= \left(\sum_{s=1}^{p}\langle O_s\rangle_2\left[\frac{\mathrm{i}}{2}\langle O_s\rangle_1\omega_s\,\mathrm{d}t-\sqrt{-i\omega_s}\,\mathrm{d}W_s(t)\right]+\frac{2\mathrm{i}}{n^2}\,\mathrm{d}t\right)c^{(2)}_{n,l,m,\tau}(t)\\
&\quad-\left(\sum_{s=1}^{p}[\mathrm{i}\langle O_s\rangle_1\omega_s\,\mathrm{d}t-\sqrt{-\mathrm{i}\omega_s}\,\mathrm{d}W_s(t)]\right)\sum_{n',l',m'}\langle n,l,m|O_s|n',l',m'\rangle c^{(2)}_{n',l',m',\tau}(t)\\
&\quad-\left(\sum_{s=1}^{p}|\omega_s|\frac{\langle\phi_2|\phi_2\rangle\left[\langle O_s^{\dagger}O_s\rangle_2-|\langle O_s\rangle_2|^2\right]}{2\mathrm{Re}\{\langle\phi_1|\phi_2\rangle\}}\,\mathrm{d}t\right)c^{(1)}_{n,l,m,\tau}(t),
\end{aligned}\tag{28}$$

where we calculate expectations via formulae such as

$$\langle\phi_1|O_s|\phi_1\rangle=\sum_{\tau}\sum_{n,l,m}\sum_{n',l',m'}c^{(1)*}_{n,l,m,\tau}(t)\langle n,l,m|O_s|n',l',m'\rangle c^{(1)}_{n',l',m',\tau}(t).$$

An initial state consisting of random mixtures of 1s and 2s He^+ basis functions for each electron was chosen. We chose a basis set with $n_{\max}=4$ to perform the calculations. Equations (28) were solved using an order 4.5 variable time-step (i.e., adaptive) Runge–Kutta method which has been specifically developed to solve such stochastic differential equations [14, 15].

A detailed discussion of the computational method will be presented elsewhere [15]. In figures 1 and 2 we plot the real and imaginary (respectively) parts of $\langle\psi(0)|\psi(t)\rangle$ against

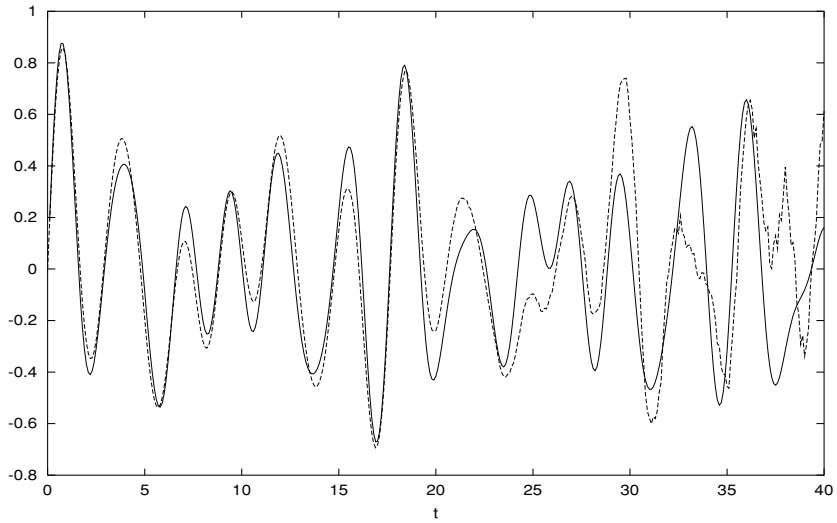

Figure 2. $\mathrm{Im}\langle\Psi(0)|\Psi(t)\rangle$ versus t.

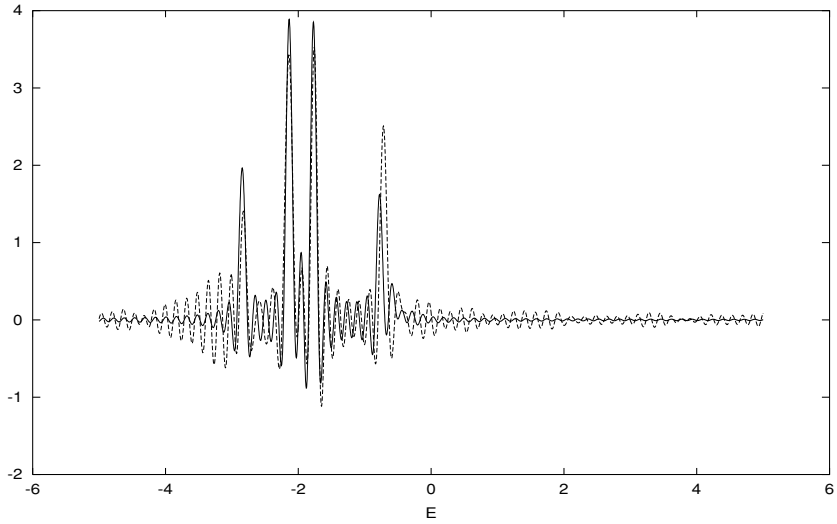

Figure 3. He energy spectrum.

time in atomic units for an exact propagation of the initial state (solid curve) and for the solution obtained via equations (28) for 200 000 realizations (dashed curve). The agreement is satisfactory although the calculation has not completely converged. In figure 3, we show the energy spectrum calculated via equation (8) for the exact and stochastic wave solutions. Again agreement is good with the stochastic calculation reproducing all energy levels.

6. Extension to bosons

Stochastic decompositions for pairwise interactions are also of interest for bosons in the context of Bose–Einstein condensation [5]. Here we show that our approach can be adapted to bosons as well as fermions.

To begin with consider the case of two pairwise interacting bosons. Again we break the *general* initial wavefunction into a sum of symmetric states of the form $|\Psi(0)\rangle = \beta(|\phi_1(0)\rangle|\phi_2(0)\rangle + |\phi_2(0)\rangle|\phi_1(0)\rangle)$. We need an exact means of propagating the single-particle states individually such that

$$|\Psi(t)\rangle = \beta M[|\phi_1(t)\rangle|\phi_2(t)\rangle + |\phi_2(t)\rangle|\phi_1(t)\rangle], \tag{29}$$

where $|\phi_1(t)\rangle$ and $|\phi_2(t)\rangle$ satisfy norm-preserving stochastic wave equations. To do this we add a fictitious subsystem of two spin-1/2 degrees of freedom with null Hamiltonian and anti-symmetric state $(1/\sqrt{2})(|+\rangle|-\rangle - |-\rangle|+\rangle)$ to our problem. We thus have a total wavefunction

$$\begin{aligned}|\Psi_{\rm fict}(t)\rangle &= (\beta/\sqrt{2})M[|\phi_1(t)\rangle|\phi_2(t)\rangle + |\phi_2(t)\rangle|\phi_1(t)\rangle] \otimes (|+\rangle|-\rangle - |-\rangle|+\rangle) \\ &= (\beta/\sqrt{2})M[(|\phi_{1+}(t)\rangle|\phi_{2-}(t)\rangle - |\phi_{2-}(t)\rangle|\phi_{1+}(t)\rangle) \\ &\quad - (|\phi_{1-}(t)\rangle|\phi_{2+}(t)\rangle - |\phi_{2+}(t)\rangle|\phi_{1-}(t)\rangle)],\end{aligned} \tag{30}$$

where $|\phi_{i\pm}(t)\rangle = |\phi_i\rangle|\pm\rangle$ for $i = 1, 2$. This wavefunction is a sum of two antisymmetric states. It is thus clear that solutions of (30) can be obtained by determining the time evolution of two-particle antisymmetric states

$$|\phi_{1\sigma_1}(t)\rangle|\phi_{2\sigma_2}(t)\rangle - |\phi_{2\sigma_2}(t)\rangle|\phi_{1\sigma_1}(t)\rangle, \tag{31}$$

for $\sigma_1, \sigma_2 = \pm$, which can be obtained with the method for fermions outlined above. Hence we can obtain (30) at the cost of including an extra 2-component spin to each single-particle state. From (30) we can get (29) by projecting the fictitious part of the solution via

$$|\Psi(t)\rangle = \tfrac{1}{\sqrt{2}}(\langle+|\langle-| - \langle-|\langle+|)|\Psi_{\rm fict}(t)\rangle.$$

Hence the 2-boson problem can be solved using the 2-fermion formalism at the expense of doubling the number of equations.

For an arbitrary number of bosons N we wish to find a stochastic decomposition

$$|\Psi(t)\rangle = \beta M\,[S|\phi_1(t)\rangle|\phi_2(t)\rangle \ldots |\phi_N(t)\rangle]$$

for dynamics generated by Hamiltonian (1) where S is the symmetrization operator. Let

$$|a\rangle = \alpha A_a|\sigma_1\rangle \ldots |\sigma_N\rangle,$$

where $|\sigma_j\rangle$ denotes one of a set of N spin states, and A_a is the anti-symmetrization operator on this space. Here α is a normalization constant. If the spins again have a null Hamiltonian then we may define a fictitious dynamics

$$|\Psi_{\rm fict}(t)\rangle = |\Psi(t)\rangle|a\rangle = \alpha\beta M[SA_a|\phi_{1\sigma_1}\rangle \cdots |\phi_{N\sigma_N}\rangle],$$

where each of the $N!$ terms $A_a|\phi_{1\sigma_1}\rangle \cdots |\phi_{N\sigma_N}\rangle$ in the symmetrization sum is antisymmetric. Here $|\phi_{j\sigma_j}\rangle = |\phi_j\rangle|\sigma_j\rangle$ and so by adding an extra fictitious spin with N allowed states we can convert the problem into fermion form. Application of the fermion method is then straightforward and the boson wavefunction can be extracted in the end by projecting out the fictitious spin state via $|\Psi(t)\rangle = \langle a|\Psi_{\rm fict}(t)\rangle$. Because of the need to introduce a fictitious spin, the computational costs of the boson method scale between $O(N^3)$ and $O(N^6)$ depending on the nature of the interaction.

7. Summary

We have shown that the time-dependent quantum N-body problem for pairwise interacting fermions can be exactly decomposed into N one-body problems each of which obeys a stochastic norm-conserving wave equation. Our approach improves on previous decompositions [6] because the single-particle equations conserve norm and thus are much more stable numerically. Use of the method was demonstrated by calculating the low energy spectrum of helium. We have also explained how the approach can be extended to bosons.

Acknowledgments

The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada. LT acknowledges the support of Projecto 4.17 of the CIC of Universidad Michoacana (Mexico).

Appendix

Consider the single-particle Hamiltonian $H = -\hbar^2\nabla^2/2m_e - Ze^2/r$ which has hydrogen-like eigenfunctions of form (27) with

$$R_{n,l}(r) = \frac{2}{n^2}\sqrt{Z^3\frac{(n-l-1)!}{(n+l)!}}\,\mathrm{e}^{-Zr/n}\left(\frac{2Zr}{n}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right)$$

in atomic units with associated energies $E_n = -Z^2/2n^2$. It can then be shown that

$$\begin{aligned}
\langle\psi_{n_1,l_1,m_1}(1)\psi_{n_2,l_2,m_2}(2)|\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}|\psi_{n_1',l_1',m_1'}(1)\psi_{n_2',l_2',m_2'}(2)\rangle &= \frac{Z}{16}\sqrt{\frac{(2l_1'+1)(2l_2'+1)}{(2l_1+1)(2l_2+1)}}\\
&\times\sqrt{\frac{(n_1-l_1-1)!(n_1'-l_1'-1)!(n_2-l_2-1)!(n_2'-l_2'-1)!}{(n_1+l_1)!(n_1'+l_1')!(n_2+l_2)!(n_2'+l_2')!}}\\
&\times\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-1)^m\begin{bmatrix}l_1' & l & l_1\\ m_1' & m & m_1\end{bmatrix}\begin{bmatrix}l_2' & l & l_2\\ m_2' & -m & m_2\end{bmatrix}\begin{bmatrix}l_1' & l & l_1\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}l_2' & l & l_2\\ 0 & 0 & 0\end{bmatrix}\\
&\times\sum_{k_1=0}^{n_1-l_1-1}\sum_{k_1'=0}^{n_1'-l_1'-1}\sum_{k_2=0}^{n_2-l_2-1}\sum_{k_2'=0}^{n_2'-l_2'-1}(-1)^{k_1+k_1'+k_2+k_2'}\\
&\times\frac{(l_1+l_1'+l_2+l_2'+k_1+k_1'+k_2+k_2'+4)!}{k_1!k_1'!k_2!k_2'!}\binom{n_1+l_1}{n_1-l_1-1-k_1}\\
&\times\binom{n_1'+l_1'}{n_1'-l_1'-1-k_1'}\binom{n_2+l_2}{n_2-l_2-1-k_2}\binom{n_2'+l_2'}{n_2'-l_2'-1-k_2'}\\
&\times\frac{(2/n_1)^{k_1+l_1+2}(2/n_1')^{k_1'+l_1'+2}(2/n_2)^{k_2+l_2+2}(2/n_2')^{k_2'+l_2'+2}}{\left(1/n_1+1/n_1'+1/n_2+1/n_2'\right)^{l_1+l_1'+l_2+l_2'+k_1+k_1'+k_2+k_2'+5}}\\
&\times\left[\frac{1}{l+l_1+l_1'+k_1+k_1'+3}F\left(1,l_1+l_1'+l_2+l_2'+k_1+k_1'+k_2+k_2'+5;\right.\right.\\
&\left.l+l_1+l_1'+k_1+k_1'+4;\frac{1/n_1+1/n_1'}{1/n_1+1/n_1'+1/n_2+1/n_2'}\right)\\
&+\frac{1}{l+l_2+l_2'+k_2+k_2'+3}F\left(1,l_1+l_1'+l_2+l_2'+k_1+k_1'+k_2+k_2'+5;\right.\\
&\left.\left.l+l_2+l_2'+k_2+k_2'+4;\frac{1/n_2+1/n_2'}{1/n_1+1/n_1'+1/n_2+1/n_2'}\right)\right],
\end{aligned}$$

where $F(a,b;c;d)$ is the hypergeometric function [11]. Here

$$\begin{bmatrix}j_1 & j_2 & j\\ m_1 & m_2 & m\end{bmatrix} = \langle j_1, j_2, m_1, m_2|j,m\rangle$$

denote the Clebsch–Gordon coefficients. We have used the convention of [13] in which

$$\begin{bmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{bmatrix} = \delta_{m,m_1+m_2}\sqrt{(2j+1)AB}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!C_n} \tag{A.1}$$

with

$$A = \frac{(j_1+j_2-j)!(j+j_1-j_2)!(j+j_2-j_1)!}{(j+j_1+j_2+1)!}$$

$$B = (j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j+m)!(j-m)!$$

$$C_n = (j_1+j_2-j-n)!(j_1-m_1-n)!(j_2+m_2-n)!(j-j_2+m_1+n)!(j-j_1-m_2+n)!,$$

where it is understood that the sum in (A.1) truncates when factorials have negative arguments.

References

[1] Maitra N T, Burke K, Appel H, Gross E K U and van Leeuwen R 2002 *Reviews of Modern Quantum Chemistry* vol II (Singapore: World Scientific)

[2] Berlin Y A, Hutchison G R, Rempala P, Ratner M A and Michl J 2003 *J. Phys. Chem.* A **107** 3970 and references therein

[3] Koonin S E, Dean D J and Langanke K 1997 *Phys. Rep.* **278** 1

[4] Gisin N and Percival I C 1992 *J. Phys. A: Math. Gen.* **25** 5677

[5] Carusotto I and Castin Y 2003 *Laser Phys.* **13** 509
Carusotto I, Castin Y and Dalibard J 2001 *Phys. Rev.* A **63** 023606

[6] Juillet O and Chomaz Ph 2002 *Phys. Rev. Lett.* **88** 142503

[7] Wilkie J 2003 *Phys. Rev.* E **67** 017102

[8] Sugiyama G and Koonin S E 1986 *Ann. Phys. (NY)* **168** 1
Charutz D M and Neuhauser D 1994 *J. Chem. Phys.* **102** 4495

[9] See for example Messiah A 1999 *Quantum Mechanics* (New York: Dover)

[10] Hasegawa H and Ezawa H 1980 *Suppl. Prog. Theor. Phys.* **69** 11
Gardiner C W 1983 *Handbook of Stochastic Methods* (Berlin: Springer)

[11] Gradshteyn I S and Ryzhik I M 2000 *Table of Integrals, Series, and Products,* 6th edn (San Diego, CA: Academic)

[12] Landau L D and Lifshitz E M 2002 *Quantum Mechanics,* 3rd edn (Oxford: Butterworth-Heinemann)

[13] Devanathan V 1999 *Angular Momentum Techniques in Quantum Mechanics* (Dordrecht: Kluwer)

[14] Wilkie J 2004 *Phys. Rev.* E **70** 017701

[15] Wilkie J and Çetinbaş M submitted