Chemical Physics Letters 653 (2016) 60–66

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

A new version of fermion coupled coherent states method: Theory and applications in simulation of two-electron systems

Mohammadreza Eidi [a,b], Mohsen Vafaee [a,*], Ali Reza Niknam [b], Nader Morshedian [c]

[a] Department of Chemistry, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran
[b] Laser and Plasma Research Institute, Shahid Beheshti University, G.C., Tehran, Iran
[c] Research School of Plasma and Nuclear Fusion, NSTRI, P.O. Box 14399-51113, Tehran, Iran

ARTICLE INFO

Article history:
Received 9 February 2016
Revised 12 April 2016
In final form 13 April 2016
Available online 16 April 2016

ABSTRACT

We report a new version of fermion coupled coherent states method (FCCS-II) to simulate two-electron systems based on a self-symmetrized six-dimensional (6D) coherent states grid. Unlike the older fermion coupled coherent states method (FCCS-I), FCCS-II does not need any new equations in comparison with the coupled coherent states method. FCCS-II uses a simpler and more efficient approach for symmetrizing the spatial wave function in the simulation of fermionic systems. This method, has significantly increased the speed of computations and give us the capability to simulate the quantum systems with the larger CS grids. We apply FCCS-II to simulate the Helium atom and the Hydrogen molecule based on grids with a large numbers of coherent states. FCCS-II with a relatively low number of CS gives a potential energy curve for H_2that is very close to the exact potential curve. Moreover, we have re-derived all the important equations of the FCCS-I method.

1. Introduction

During the last two decades, the coupled coherent states (CCS) method has been developed for simulating the quantum dynamics of high-dimensional systems by solving the time dependent Schrödinger equation (TDSE) in the phase space based on coherent states [1–13]. Two of other trajectory-guided approaches are the variational multi-configurationalGaussian approach (vMCG) [7,14–16] and the multiple spawning (MS) method [7,16,17]. vMCG uses time-dependent Gaussian functions as the basis set. Basis sets which obey vMCG equations, do not follow classical trajectories. The equations of vMCG are derived from the variational principle [7]. Therefore, vMCG potentially have the ability to get the best possible solution of the Schrödinger equation. Although, the vMCG equations are complicated and numerically expensive, but vMCG method is able to directly describe quantum events such as tunneling and passage through a conical intersection and at the same time the convergence is fast. vMCG method provides a good description of the dynamics of a molecular system using only a small basis set and subsequently a small number of parameters [16]. MS uses a quantum mechanical wavepacket described by a superposition of Gaussian basis functions that unlike vMCG follows classical trajectories. Hence, MS would not be a good choice for simulating two-electron systems. Also, MS have a great ability to manage the size of the basis set when required [16,18]. As for MS, the vMCG method has been successfully applied in the context of non-adiabatic photochemistry and it appears to be a quite reliable, efficient and cheap approach to deal with non-adiabatic transitions between coupled electronic states while keeping the advantage of calculating the potential energy surfaces (PES) and non-adiabatic couplings on-the-fly [16]. The CCS methodology is situated between vMCG and MS. The CCS method has many considerable advantages which distinguish it from other trajectory guided approaches. The main advantage is that fewer configurations are needed for simulating a system with large number of degrees of freedom. Another advantage is that, the singularity of the Coulombic potentials can be removed and replaced by an error function [5,9]. For more information about the main concepts of the CCS method see Refs. [4,7].

The investigation of non-perturbative laser induced phenomena in many-electron atoms and molecules, such as non-sequential double ionization (NSDI) and high-order harmonic generation (HHG) has formed a growing area of research [19,20]. In multi-electron atoms, He provides the only conceivable meeting ground between ab initio theory and experiment in multiple ionization of atoms by the intense laser fields [19]. Simulation of He exposed to an intense laser field with the wavelength near 800 nm (most frequently used in experiments) and comparison of simulation results with the experiments has not been accomplished yet [19].

* Corresponding author.
E-mail address: m.vafaee@modares.ac.ir (M. Vafaee).

http://dx.doi.org/10.1016/j.cplett.2016.04.054
0009-2614/

Some ab initio TDSE calculations beyond the one dimensional (1D) approximation for the interaction of He and H_2 with intense few-cycle near-infrared laser pulses have been reported by Parker et al. [21] and Ruiz et al. [22], respectively. Belfast group performed this comparison under a linearly polarized laser field for a shorter wavelength at 390 nm [21]. However, most computations are carried out for two-electron systems considering one dimension for each electron, and with classical [23–26] and quantum [27] nuclear dynamics. Full dimensional study of two-electron systems like He and H_2 in the presence of an intense laser field is not possible yet. By developing the CCS method, it is hoped that solving this major problem become possible.

Originally, the CCS method has been developed to treat the motion of distinguishable particles. For simulating the dynamics of fermion particles, a modified version of the CCS method has been introduced by Kirrander and Shalashilin as fermion coupled coherent states (FCCS) [11]. We have labeled this Shalashilin's approach as FCCS-I throughout this article. The CCS and FCCS-I methods have tried to develop a useful tool for simulating atomic and molecular systems in full dimensions and investigating the dynamics of electrons in systems interacting with intense laser radiation and related phenomena. Some simulations performed by CCS and FCCS-I methods can be listed as follows: the 6D simulation of H_2 and its electronic states by the standard CCS [5,6], simulation of He double ionization [9], the strong-field ionization of He at long wavelengths [10], electron dynamics in the laser fields by the FCCS-I method on the base of Frozen Gaussians [11], high-order harmonic generation by the CCS approach [13] and other reported applications [28–34]. Another work done by Zhou and Chu [12] is the full dynamics of H_2 in intense linearly polarized laser fields which in fact used the Heller's Frozen Gaussians method instead of the CCS method.

In the simulations reported on the basis of the CCS and the FCCS-I methods, high energy coherent states are excluded from the grid. Therefore, the grid is biased to the regions with the lowest energy [6]. Furthermore, the diffusion Monte-Carlo (DMC) method on the basis of these two methods has needed a grid refinement algorithm like the maximizing the residual overlap (MRO) [6]. Moreover, the FCCS-I method uses a symmetrizing equation that makes equations complex and computations cumbersome. Here, we introduce a new version of fermion coupled coherent states method. We have labeled this version of FCCS as FCCS-II throughout this article. This new version of FCCS method does not need to use any additional symmetrizing equation, biasing the grid to the regions with the lowest energy and any grid refinements.

In this article, after giving a brief review on the CCS and the FCCS-I methods, we introduce FCCS-II method. In Section 2.1, coherent states and the CCS method have been investigated and reviewed in a new manner. In Section 2.2, we have studied the FCCS-I method and proposed FCCS-II method. Moreover, in Section 2.1, we have employed a new random coherent states grid generation method which considers two compression parameters for position and momentum coordinates in the phase space. In Section 2.3, the diffusion Monte-Carlo and imaginary time propagation methods has been introduced for FCCS-II method. Finally, we have applied the FCCS-II method to simulate the ground state of He and the potential well of H_2 in Section 3.

2. Theory

2.1. The coupled coherent states method (CCS)

We give a brief review of basics of coherent states and the CCS method. In this part, some important equations of the CCS method [4,7]. will be re-derived. Coherent states (CS) are eigenkets of the annihilation operator $\hat{a}$ and eigenbras of the creation operator $\hat{a}^\dagger$ as

$$\begin{aligned} a|Z\rangle &\equiv Z|Z\rangle \\ \langle Z|a^\dagger &\equiv \langle Z|Z^* \end{aligned} \tag{1}$$

where eigenvalue Z have this form

$$Z = \frac{\gamma^{1/2}}{\sqrt{2}}q + i\frac{\gamma^{-1/2}}{\sqrt{2}\hbar}p \tag{2}$$

where q is the position and p is the momentum of the wave packet with fixed coordinate space width γ. We can name this CS as standard (asymmetric) coherent state (ACS) compared to the symmetrized coherent states that will be named as SCS in the next section. Coherent states construct a nonorthogonal overcomplete basis set as

$$\langle Z|Z'\rangle = \prod_{j=1}^{M} exp\left(-\frac{1}{2}\left(|z_j|^2 + \left|z'_j\right|^2\right) + z_j^* z'_j\right). \tag{3}$$

For a two-electron system, M, the number of dimensions, is equal to six. The Hamiltonian operator $\widehat{H}\left(\widehat{P},\widehat{Q}\right)$ can be expressed in the terms of the creation and the annihilation operators $\widehat{H}(\hat{a},\hat{a}^\dagger)$. The Hamiltonian operator $\widehat{H}(\hat{a},\hat{a}^\dagger)$, can be reordered in such a way that all creation operators place on the left $\widetilde{H}(\hat{a}^\dagger,\hat{a})$. The matrix elements of the ordered Hamiltonian operator $\widetilde{H}(\hat{a}^\dagger,\hat{a})$ can be easily derived by the use of Eq. (1). Then, we have

$$\langle Z|\widetilde{H}(\hat{a}^\dagger,\hat{a})|Z'\rangle = \langle Z|Z'\rangle\widetilde{H}(Z^*,Z'). \tag{4}$$

Identity operator of coherent states has this form

$$\mathbb{I} = \sum_{k,l=1}^{N} |Z_k\rangle\left(\Omega^{-1}\right)_{kl}\langle Z_l|. \tag{5}$$

where N is the number of CS. In Eq. (5), Ω^{-1} is the inverse of the overlap matrix Ω with elements

$$\Omega_{kl}(t) = \langle Z_k(t)|Z_l(t)\rangle. \tag{6}$$

In the coordinate representation, these M dimensional coherent states are Gaussian wave packets with fixed width γ [8]

$$\langle X|Z\rangle = \prod_{j=1}^{M}\left(\frac{\gamma_j}{\pi}\right)^{1/4} exp\left(-\frac{\gamma_j}{2}\left(x^{(j)}-q^{(j)}\right)^2 + \frac{i}{\hbar}p^{(j)}\left(x^{(j)}-q^{(j)}\right) + \frac{ip^{(j)}q^{(j)}}{2\hbar}\right). \tag{7}$$

Wave function of a system with M degrees of freedom can be represented as a superposition of N trajectory-guided coherent states

$$|\psi(t)\rangle = \sum_{k=1}^{N} D_k(t) exp\left(i\frac{S_k(t)}{\hbar}\right)|Z_k(t)\rangle. \tag{8}$$

This is the main idea of the CCS method [4,7,11]. In the Eq. (8), preexponential factor $D_k(t)$ can be derived by

$$D_k(t) = \sum_{l=1}^{N} C_l(t) exp\left(i\frac{(S_l(t)-S_k(t))}{\hbar}\right)\left(\Omega^{-1}\right)_{kl}(t) \tag{9}$$

where

$$C_l(t) = \langle Z_l(t)|\psi(t)\rangle exp\left(-\frac{i}{\hbar}S_l(t)\right). \tag{10}$$

In Eqs. (9) and (10), $S(t)$ is the classical action

$$S(t) = \int \ell dt. \tag{11}$$

where ℓ is the diagonal matrix elements of the Lagrangian operator in the representation of coherent states