

Time-dependent optimized coupled-cluster method for multielectron dynamics

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We present a working implementation of a simplified version of the orbital-adaptive time-dependent coupled-cluster method which we refer to as just the time-dependent coupled-cluster (TDCC) method. OAT-DCC/TDCC approximates solutions to the quantum N -body problem and for $N = 2$ TDCC is equivalent to the time-dependent configuration-interaction method (TDCI). A TDCI solver is implemented and shown to be correct by comparing with a previous study and is then used as a foundation for verifying the implementation of the TDCC method. For one and two dimensional quantum dot systems with $N = 2$ we demonstrate that the methods are equal to numerical precision. Furthermore, for a small number of basis functions we use the TDCC solver to compute the time evolution of six-electron isotropic quantum dot.

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I. INTRODUCTION

Quantum mechanics is a theory that describes/models the properties of microscopic systems. It postulates that given the so-called wavefunction, $\Psi(\mathbf{r}, t)$, we can in principle compute all that there is to know about the system. Given suitable initial conditions $\Psi(\mathbf{r}, t)$ can be determined for all future time by solving the time-dependent Schrödinger equation (TDSE),

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t). \quad (1)$$

The initial condition is typically taken as a linear combination of what is called stationary states, which in turn can be found by solving what is known as the time-independent Schrödinger (TISE) equation

$$\hat{H} \Psi(\mathbf{r}) = E \Psi(\mathbf{r}). \quad (2)$$

Exact/analytical solutions to the TISE is possible only for the simplest systems and general solutions to the TDSE is even rarer. Thus, one must resort to approximative/numerical methods. Of particular interest is the so-called many-body problem where one considers systems of a large number of interacting particles, where large can be anywhere from two to infinity.

Several approaches for solving the many-body TISE numerically/approximatively has been devised such as Hartree-Fock (HF), Density Functional Theory (DFT), Configuration Interaction (CI) and Coupled Cluster (CC). While efficient, Hartree-Fock and DFT are insufficient if one wants a high degree of accuracy. Configuration Interaction and Coupled Cluster methods are hierarchical in the sense that one can systematically construct increasingly accurate approximations. If the CI method is not truncated we have what is known as Full Configuration Interaction (FCI). FCI can be seen as exact (within

some finite space), however it suffers from exponential scaling. Truncated CI methods which would achieve polynomial scaling are problematic since they are not size-consistent and extensive. Truncated CC methods on the other hand are size-consistent and extensive and achieves polynomial scaling. Due to this fact Coupled Cluster is considered the gold standard of many-body techniques if high accuracy is desired.

Similarly, there exists different approximations to the solution of the TDSE with the Multiconfiguration Time-Dependent Hartree-Fock method (MCTDHF) being considered the most accurate. MCTDHF, which is combination of CI and HF generalized to the time domain, suffers from exponential scaling. In a recent article¹, Simen Kvaal proposes a method based on Coupled-Cluster theory, the so-called Orbital Adaptive Time Dependent Coupled Cluster method (OATDCC), which is a hierarchical approximation to the MCTDHF method. The OATDCC inherits size-consistency and extensivity from the CC method and achieves polynomial scaling.

II. THEORY/FORMALISM

A. The model Hamiltonian

We shall model the quantum dot systems as a collection of N nonrelativistic electrons of mass m in d -dimensional space trapped by a confining potential $v_{\text{conf}}(\hat{\mathbf{r}})$. Here $\hat{\mathbf{r}}$ is the position operator in d -dimensional space

$$\hat{\mathbf{r}} \equiv \sum_{i=1}^d \hat{\mathbf{x}}_i \hat{\mathbf{e}}_i \quad (3)$$

with $\hat{\mathbf{e}}_i$ a unit vector.

The electrons interact through the Coulomb interaction $e^2/(4\pi\epsilon R)$, where e is the electron charge, ϵ the permittivity of the medium and R is the distance between two interacting electrons.

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For convenience, we will use atomic units, chosen such that $\hbar \equiv m \equiv e \equiv 4\pi\epsilon \equiv 1$. Thus, all energies are presented in hartrees per \hbar .

In atomic units, the many-body problem is described by the Hamiltonian on second quantized form

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = \sum_{pq} \langle p|\hat{h}_0|q \rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \langle pq|\hat{u}|rs \rangle_{\text{AS}} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \quad (4)$$

where \hat{H}_1 and \hat{H}_2 are its one- and two-body parts.

The operator \hat{h}_0 is the single-particle Hamiltonian

$$\hat{h}_0 = -\frac{1}{2}\nabla^2 + v_{\text{conf}}(\mathbf{r}) \quad (5)$$

while \hat{u} represents the Coulomb interaction. Here $|p\rangle$ is a single-particle basis function which in its position representation is given by

$$\langle \mathbf{r}|p \rangle \equiv \phi_p(\mathbf{r}). \quad (6)$$

In practice, we have to choose some single-particle basis to compute within. One typical choice is to take the single-particle basis to be the eigenfunctions of \hat{h}_0 such that

$$\hat{h}_0 |p\rangle = \epsilon_p |p\rangle, \quad (7)$$

where ϵ_p is the corresponding eigenvalue.

The quantities $\langle p|\hat{h}_0|q \rangle$ and $\langle pq|\hat{u}|rs \rangle_{\text{AS}}$ are referred to as *matrix elements* and must be computed relative to the chosen single-particle basis. In particular, $\langle pq|\hat{u}|rs \rangle_{\text{AS}}$ are *antisymmetrized* matrix elements, defined by

$$\langle pq|\hat{u}|rs \rangle_{\text{AS}} \equiv u_{rs}^{pq} - u_{sr}^{pq} \quad (8)$$

where u_{rs}^{pq} is the interaction integral,

$$u_{rs}^{pq} \equiv \int \phi_p^*(\mathbf{r}_1) \phi_q^*(\mathbf{r}_2) \hat{u}(\mathbf{r}_1, \mathbf{r}_2) \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (9)$$

In the rest of this paper we will drop the subscript AS for the antisymmetrized matrix elements.

In order to generate dynamics the electrons are coupled to a time dependent monochromatic laser field, with frequency ω and amplitude \mathcal{E}_0 , polarized along the x -axis²

$$v_{\text{laser}}(\mathbf{r}, t) = \hat{\mathbf{x}}_1 \mathcal{E}_0 \sin(\omega t), \quad (10)$$

resulting in a time dependent single-particle Hamiltonian

$$\hat{h}_t = \hat{h}_0 + v_{\text{laser}}(\mathbf{r}, t). \quad (11)$$

The choice of polarization axis is arbitrary.

The total time dependent Hamiltonian of the system is then given by

$$\hat{H}(t) = \sum_{pq} \langle p|\hat{h}_t|q \rangle \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \langle pq|\hat{u}|rs \rangle_{\text{AS}} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r. \quad (12)$$

It is important to note that this implies that we have to update the matrix elements $\langle p|\hat{h}_t|q \rangle$ during the simulation. However, in this work we consider only methods where the single-particle basis is held fixed in time, hence the two-body matrix elements can be computed $\langle pq|\hat{u}|rs \rangle$ once and for all.

We will handle the time dependent problem in two steps. First we prepare a system in its groundstate by solving the time independent Schrödinger equation (TISE) for the field-free Hamiltonian (4). Then we apply the time dependent laser field and compute the time evolution from the time dependent Schrödinger equation (TDSE). Before we discuss the methods for solving the TISE and TDSE respectively we will address the choice of single-particle basis.

B. Choice of single-particle basis

The choice of single-particle basis will in general depend on the problem. In quantum chemistry it is customary to expand the eigenfunctions, $\{\psi_k\}$, of \hat{h}_0 in (non-orthogonal) Gaussian basis functions $g_p(\mathbf{r})$

$$\hat{h}_0 |\psi_k\rangle = \hat{h}_0 \sum_{p=1}^L g_p(\mathbf{r}) = \epsilon_k \sum_{p=1}^L g_p(\mathbf{r}) \quad (13)$$

resulting in a generalized eigenvalue problem which must be solved for the eigenfunctions. Ideally we would let $L \rightarrow \infty$ but must be taken as finite in practice. The choice of Gaussian basis functions is popular due to the fact that matrix elements can be evaluated efficiently³.

Another popular choice, which is the one chosen in this work, is to use the eigenfunctions of the Harmonic oscillator (HO)

$$\left(-\frac{1}{2}\nabla^2 + \frac{1}{2}\omega_{\text{HO}}\hat{\mathbf{r}}^2 \right) \phi_k(\mathbf{r}) = \epsilon_k \phi_k(\mathbf{r}) \quad (14)$$

as a single-particle basis. The solutions to the HO-problem is well known and the eigenfunctions have closed form expressions.

Of particular importance for our purposes is the fact that the interaction integrals

$$u_{rs}^{pq} \equiv \int \phi_p^*(\mathbf{r}_1) \phi_q^*(\mathbf{r}_2) \hat{u}(\mathbf{r}_1, \mathbf{r}_2) \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (15)$$

can be solved analytically in two- and three-dimensions, using HO-basis functions in polar and spherical coordinates respectively^{4,5}. If the confining potential is chosen to be the Harmonic oscillator potential we are essentially done and can move on to the many-body treatment of the problem.

Additionally we may approximate the eigenfunctions of more general confining potentials by expanding the solutions in the HO-functions.

Consider the general problem

$$\hat{h}_0 |\psi_k\rangle = \epsilon_k |\psi_k\rangle \quad (16)$$

where

$$\hat{h}_0 = -\frac{1}{2}\nabla^2 + v_{\text{conf}}(\mathbf{r}). \quad (17)$$

Expand the eigenfunctions $|\psi_k\rangle$ in the HO-functions $|\phi_p\rangle$

$$|\psi_k\rangle = \sum_{p=1}^L c_{p,k} |\phi_p\rangle \quad (18)$$

and insert into Eq.(16). Left-projection with $\langle\phi_q|$ results in the following expression

$$\sum_{p=1}^L c_{p,k} \langle\phi_q|\hat{h}_0|\phi_p\rangle = \epsilon_k \sum_{p=1}^L c_{p,k} \delta_{q,p} \quad (19)$$

where we have used the orthogonality of the HO-functions. This can be written on matrix form as

$$HC = C\mathcal{E} \quad (20)$$

where $H_{qp} \equiv \langle\phi_q|\hat{h}_0|\phi_p\rangle$, \mathcal{E} is a diagonal matrix containing the eigenvalues on its diagonal, and C is matrix containing the expansions coefficients for basis function k in its columns. The eigenproblem must be solved for the expansions coefficients, resulting in a approximation of the interaction integrals in terms of the known interaction integrals $\langle\phi_\alpha\phi_\beta|\hat{u}|\phi_\gamma\phi_\delta\rangle$ given by

$$\langle\psi_p\psi_q|\hat{u}|\psi_r\psi_s\rangle = \sum_{\alpha\beta\gamma\delta} c_{p,\alpha}^* c_{q,\beta}^* c_{r,\gamma}^* c_{s,\delta}^* \langle\phi_\alpha\phi_\beta|\hat{u}|\phi_\gamma\phi_\delta\rangle. \quad (21)$$

The quality of such an approximation will naturally depend on how close the confining potential is to the Harmonic oscillator potential. Nevertheless it constitutes a convenient starting point for investigations of more general potentials.

C. Configuration interaction theory

1. Time independent Configuration interaction

The conceptually simplest method for solving the many-problem is probably that of Configuration interaction (CI).

Let us first consider the time independent Schrödinger equation

$$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle \quad (22)$$

where \hat{H} is the field-free Hamiltonian given by Eq. (4), $|\Psi_k\rangle$ is the many-body eigenfunction and E_k its corresponding eigenvalue. It is customary to use a (finite in practice) basis of orthogonal Slater determinants (SD), $\{\Phi_p\}_{p=1}^{N_{\text{sd}}}$ where N_{sd} is the number of determinants, built from the single-particle basis functions described in the previous section.

The principal idea of CI is to expand the wavefunction in the SD-basis

$$\hat{H} \sum_{p=1}^{N_{\text{sd}}} c_{p,k} |\Phi_p\rangle = E_k \sum_{p=1}^{N_{\text{sd}}} c_{p,k} |\Phi_p\rangle. \quad (23)$$

If we left-project with $\langle\Phi_q|$ the above equation can be written on matrix form as

$$HC = CE \quad (24)$$

where $H_{qp} \equiv \langle\Phi_q|\hat{H}|\Phi_p\rangle$, E is a diagonal matrix with the eigenvalues along its diagonal and C is a matrix containing the expansion coefficients of the k -th eigenfunction in column k . Thus if we can compute the matrix elements H_{qp} the TISE can be solved by numerical diagonalization.

The evaluation of H_{qp} is simplified by what is known as the Slater-Condon rules. If $|\Phi\rangle$ is any SD, the only non-zero contributions to H are given by

$$\langle\Phi|(\hat{H}_1 + \hat{H}_2)|\Phi\rangle = \sum_i \langle i|\hat{h}_0|i\rangle + \frac{1}{2} \sum_{ij} \langle ij|\hat{u}|ij\rangle \quad (25)$$

$$\langle\Phi|(\hat{H}_1 + \hat{H}_2)|\Phi_k^c\rangle = \langle k|\hat{h}_0|c\rangle + \sum_i \langle ki|\hat{u}|ci\rangle \quad (26)$$

$$\langle\Phi|(\hat{H}_1 + \hat{H}_2)|\Phi_{kl}^{cd}\rangle = \langle kl|\hat{u}|cd\rangle. \quad (27)$$

In other words, we only have to consider the overlap between determinants that differ by at most two occupied single-particle functions. Here we use the convention that $i, j, k, l = 1, \dots, N$, with N being the number of electrons and $a, b, c, d = N + 1, \dots$ and $p, q, r, s = 1, \dots, L$. Thus, we see that if the matrix elements $\langle p|\hat{h}_0|q\rangle$ and $\langle pq|\hat{u}|rs\rangle$ are known we can set up the Hamilton matrix and diagonalize it, obtaining the expansion coefficients C .

Ideally we would like $N_{\text{sd}} \rightarrow \infty$ which is impossible in practice. If we choose a finite number, L , of single-particle basis functions and use all the linearly independent Slater determinants we can build from this basis we get what is known as the Full Configuration Interaction (FCI). However, the problem with FCI is that the number of linearly independent determinants are given by

$$N_{\text{sd}} = \binom{L}{N} \quad (28)$$

with N being the number of electrons. This means that the numbers of SD's becomes huge very fast, making FCI practical/feasible only for the smallest systems. On the other hand, FCI is exact within a given computational space, thus it is an invaluable tool in aiding us determining the validity of more sophisticated methods. Furthermore, CI is variational in the sense that it guarantees an upper bound on the groundstate energy.

One way to adress the problems with FCI is to consider a *reference* determinant $|\Phi\rangle$, typically taken to be the

Hartree-Fock state, and consider excitations upon this state. That is, we make the ansatz

$$|\Psi\rangle = A_0 |\Phi\rangle + \sum_{ia} A_{ia} |\Phi_i^a\rangle + \frac{1}{4} \sum_{ijab} A_{ijab} |\Phi_{ij}^{ab}\rangle + \dots \quad (29)$$

where $|\Phi_i^a\rangle$ is a singly-excited determinant, $|\Phi_{ij}^{ab}\rangle$ doubly-excited etc. and truncate at some excitation level. This results in a hierarchy of approximations known as CIS (only single-excitations), CID (only double-excitations), CISD (singles and doubles and so on. In this way one obtains polynomial scaling of the number of determinants. The problem with this approach is that the truncated CI-wavefunction is not size-consistent and extensive³. It turns out that this problem is resolved by the Coupled Cluster method, which makes it the de facto standard of many-body methods today.

2. Time dependent Configuration interaction

Another advantage with CI is that it is straightforward to generalize to time dependent problems. Recall that the time evolution of an arbitrary state, $|\Psi(t)\rangle$ with initial condition $|\Psi(t_0)\rangle$, is given by the time dependent Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle. \quad (30)$$

We will take the initial condition to be some (normalized) linear combination of the CI eigenfunctions. In particular, we are interested in the time evolution of the ground-state.

The time-dependent Configuration Interaction (TDCI) method is obtained by placing a time-dependence on the expansion coefficients in the CI-wavefunction while keeping the single-particle basis fixed. Analogous to what we did in the previous section, we expand $|\Psi(t)\rangle$ in a given orthonormal Slater determinant basis $\{\Phi_p\}_{p=1}^{N_{sd}}$

$$|\Psi(t)\rangle = \sum_{p=1}^{N_{sd}} A_p(t) |\Phi_p\rangle. \quad (31)$$

If we now insert this expansion into the time-dependent Schrödinger equation we obtain,

$$i\hbar \sum_{p=1}^{N_{sd}} \frac{\partial A_p(t)}{\partial t} |\Phi_p\rangle = \sum_{p=1}^{N_{sd}} A_p(t) \hat{H}(t) |\Phi_p\rangle. \quad (32)$$

Left-projecting the above equation with $\langle\Phi_q|$ and using the orthonormality of the Slater determinants, we are left with a differential equation for each expansion coefficient $A_J(t)$ which can be written as the matrix-vector equation

$$i\hbar \frac{\partial A(t)}{\partial t} = H(t) A(t). \quad (33)$$

Here $H(t)$ is the time dependent Hamilton matrix defined in terms of its elements,

$$H_{qp}(t) = \langle\Phi_q|\hat{H}(t)|\Phi_p\rangle \quad (34)$$

and $A(t) = [A_0(t), A_1(t), \dots]$ is the vector containing the expansion coefficients. We refer to this as the time dependent Configuration Interaction (TDCI) method.

Completely analogous to the time independent case we have a hierarchy of TDCI methods defined by the Slater determinant basis. Thus we have a series of possible approximations ranging from TD-CIS to TD-FCI. If we did not have to truncate the Slater determinant basis, TD-FCI would be an exact solution to the TDSE. However, we must in practice truncate the basis and TDFCI suffers from the fact that the size of FCI-space grows exponentially. In order to obtain a good approximation to the exact solution we would need a huge fixed basis¹.

On the other hand it is quite straightforward to implement, especially when a program for computing the CI-groundstate already has been written. Again, the fact that the CI and CC space are equivalent for $N = 2$ makes it worthwhile to write a TDCI program, which we can use to compare with the time dependent Coupled Cluster method which we discuss in the next chapter.

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