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Comparing Models of Many Electron Quantum Dynamics

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INTRODUCTION

We are concerned with approximations of the many body problem of nonrelativistic quantum dy namics of N interacting electrons. One would ide ally like to solve the N body time dependent lin ear Schrödinger equation (TDLSE) with Coulomb potential and a time dependent external potential $V(\mathbf{r}_j, t)$ which reads,

$$i\frac{\partial}{\partial t}\Psi = \sum_{j=1}^{N}\Big(-\tfrac{1}{2}\Delta_{\mathbf{r}_j}\Psi + V(\mathbf{r}_j,t)\Psi\Big) + \sum_{1\le j<k\le N}\frac{1}{|\mathbf{r}_j-\mathbf{r}_k|}\Psi \qquad (1)$$

in atomic units. Here $\mathbf{r}_j \in \mathbb{R}^3$ denotes the position coordinates of the j^{th} particle. Although (1) is a linear PDE, it scales quite unfavourable with increasing number of particles which makes it prac tically impossible to compute solutions directly for systems with more than a few electrons.

To avoid this problem, often coupled systems of nonlinear Schrödinger equations for several single electron "orbitals" are used in practice. One way to obtain such simplified models from (1) is by "variational approximation". This technique pro duces the time dependent Hartree Fock (TDHF) or *multiconfiguration* time dependent Hartree Fock (MCTDHF) sytems and a large variety of other pos sibilities [9]. A different approach is time dependent density functional theory (TDDFT) which produces the time dependent Kohn Sham system [10] and [1].

In this work we will focus on models derived by the "variational approximation" approach namely the TDHF and MCTDHF system.

THE MCTDHF EQUATIONS

To illustrate the method we consider the 2 particle MCTDHF ansatz

$$\Psi(x_1,x_2) = \sum_{j,k=1}^{n} a_{jk}\phi_j(x_1)\phi_k(x_2), \qquad (2)$$

where $\{\phi_1,\phi_2,\dots,\phi_n\}$ is an orthonormal set of $n \ge 2$ orbitals. The coefficients satisfy $a_{kj} = -a_{jk}$ so that Ψ is antisymmetric, thus obeying Pauli's exclusion principle, and $\sum |a_{jk}|^2 = 1$ to ensure $\|\Psi\| = 1$.

The Dirac Frenkel variational principle yields a system of ordinary differential equations for the coefficients a_{jk}, coupled to a system of partial differential equations for the orbitals ϕ_i which reads in vector notation for $\vec{\phi} = (\phi_1,\phi_2,\dots,\phi_n)^T$

$$\frac{d}{dt}a_{jk} = -i\Big\langle \phi_j(x_1)\phi_k(x_2), V\Psi(x_1,x_2)\Big\rangle \qquad \forall j,k \quad (3)$$

$$\frac{d}{dt}\vec{\phi} = \frac{i}{2}(\Delta\otimes I_n)\vec{\phi} - i((I-P)\otimes\Gamma^{-1}\overline{A})V_{\vec{\phi}}(\Psi)\ . \quad (4)$$

Here A is the antisymmetric coefficient matrix and $\Gamma = \overline{A}A^T$. P is the projection onto the subspace spanned by the orbitals ϕ_i, $V_{\vec{\phi}}(\Psi)$ denotes the vector $(V_{\phi_1}(\Psi),\dots,V_{\phi_n}(\Psi))^T$, where $V_{\phi_j}(\Psi)$ is defined by

$$\langle \xi, V_{\phi_j}(\Psi)\rangle = \int \overline{\xi(x_1)\phi_j(x_2)}V(x_1,x_2)\Psi(x_1,x_2)dx_1dx_2$$

for all $\xi \in \mathcal{H}$.

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OUR GOALS AND (NUMERICAL) METHODS

We want to contribute to a better understanding of the derivation of these models (cf. [5], [3] and to to understand their interrelationships as part of a model hierarchy.

We carry out numerical tests to study systemat ically how the (MC)TDHF models perform in the context of computationally feasible "toy" problems, compared to the linear N particle Schrödinger equa tion.

It is basically impossible to estimate "a priori" which of the models in the hierarchy is "better" for the calculation of a certain quantity for example it is well known that sometimes the simple Hartree approximation gives better results than the more so phisticated Hartree Fock equation, especially when "correlation" effects play a role that are ignored by definition in the TDHF method. (cf e.g. [3] and [8]).

Clearly, MCTDHF is the canonical way to im prove the TDHF method and should, with increasing number of configurations, converge to the solutions of the N body TDLSE.

However, the proof of convergence of solutions of MCTDHF to the solutions of the time dependent N body SE (in some appropriately defined trace norm, cf. [5], [3] is still completely open. Let us remark that for MCTDHF all basic mathematical questions are open, starting with existence of unique solutions (cf. [4]) up to questions of how going beyond the Born Oppenheimer approximation of "static ions" (cf. e.g. [7]).

We state recent results of mathematically oriented papers in a way that is understandable also for physicists and (quantum) electrical engineers and we study numerically convergence of certain phys ically interesting quantities, like charge densities or "correlation" according to the new definition [8].

To calculate numerical solutions of the MCTDHF equations is not trivial, since it requires the solution of a nonlinear system of ODEs for the coefficients $a_{jk}(t)$ coupled to the evolution equations for the "orbitals" $\phi_i(\mathbf{r}, t)$.

In order to solve the MCTDHF equations (as well as the TDHF equations) we use a time splitting spectral scheme which was originally developed for the cubic NLS [2] and which has been proven to be a very efficient tool for very general classes of NLS (e.g. [1], [6]).

Using Born von Karman periodic boundary con ditions on a sufficiently large domain of calculation fits well with the trigonometric spectral method for the free evolution that is split in time from the nonlinear potential part that yields an ODE that is solved by a fourth order Runge Kutta scheme.

We present simulations for a 2 electron system in 1 space dimension where all equations of the hier archy, including the N body TDSE, can be solved relatively easily.

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