

The multi-configuration electron–nuclear dynamics method

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ABSTRACT

An approach to the correlated quantum dynamics of electrons and nuclei is proposed. It is an ab initio method, based on a multi-configuration expansion of the full molecular wave function. The objective of this development is to be able to describe the correlated motion of electrons in molecules beyond the fixed-nuclei approximation. Neither potential energy surfaces nor diabatic couplings need to be calculated, and Pulay forces do not appear. The method is illustrated by application to the $12 + 1$ dimensional LiH molecule.

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1. Introduction

In this Letter, the outline of a theory for the correlated ab initio quantum dynamics of electrons and nuclei is presented. The purpose of this theory is to describe the correlated motion of electrons and nuclei in a combined wave packet picture, that does not require the calculation of potential energy surfaces or diabatic couplings. Further, the method requires only the molecular Hamiltonian with Coulomb interactions as input, and is designed to avoid the appearance of Pulay forces.

The ansatz is derived from the Multi-Configuration Time-Dependent Hartree (MCTDH) [1–6] and Multi-Configuration Time-Dependent Hartree–Fock (MCTDHF) [7–14] methods. Both methods have been used for years for quantum dynamical calculations for either nuclei or electrons. It is straight forward to write down a mixed wave function, that contains an antisymmetric part for the electrons, and a non-symmetric part for the nuclei. The challenge here lies in the combination of the different kinds of primitive bases, namely atom centered Gaussian Type Orbitals (GTOs) for electrons [15] with a grid or DVR basis for nuclei. If the position of the atoms change, then usually also the atoms centers of the GTOs move, leading to a time-dependent basis set superposition error, which is the origin of the so called Pulay forces [16,17]. It will be shown below, that this can sometimes be avoided. The resulting theory is applicable to small molecules, and may be expected to contribute to at least two fields of research: First, simulations of correlated electron dynamics have so far been mostly in the fixed nuclei approximation. In fact, the present approach has been motivated by the desire to study the dephasing effect that the motion of the nuclei has upon an excited electron system. Second, there is the opportunity for highly accu-

rate simulations, against which more approximate methods of quantum dynamics of molecular dynamics can be tested.

Combined treatments of nuclei and electrons exist for quite some time. Electronic structure calculations have, e.g., been extended to the quantum description of hydrogen nuclei in the nuclear-electronic orbital (NEO) method by Hammes-Schiffer et al. [18–20]. Their NEO–MCSCF approach [18] uses an ansatz for the wave function which is similar to the one proposed in this Letter. However, NEO is designed to solve the time-independent Schrödinger equation by iterative methods, while our solution of the time-dependent Schrödinger equation is an initial value problem. Second, whereas the electron–nuclear correlation is usually tiny in the ground state of a molecule, qualitative new features are added to dynamic processes. Another close connection of the present work exists to the electron–nuclear dynamics (END) method of Öhrn and coworkers [21–25]. However, to our knowledge, all practical calculations have been with atoms as classical particles, and electrons on the Hartree–Fock level of theory, although potentially their theory contains the exact solution. In this work the multi-configuration expansion of the combined wave function is employed, so that the method presented here is appropriately termed multi-configuration electron–nuclear dynamics (MCEND). Furthermore, connections to other methods, such as ab initio molecular dynamics [26–29], non-adiabatic quantum dynamics [30–34], and some model calculations [35,36] exist, but cannot be discussed here in detail. Conceptually, MCEND is especially suited to describe the first excitation step in a quantum dynamical simulation, if this involves a laser pulse. If much longer propagation times are required, it will be advantageous to continue the simulation with one of the methods mentioned above.

The Letter is organized as follows. Section 2 provides the general formulation of the theory. In Section 3 some illustrative calculations are given, which serve as a proof of concept. For these, the LiH molecule with $12 + 1$ degrees of freedom has been chosen. Section 4 summarizes, and gives an outlook on future work and

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open questions. Atomic units are used throughout, if not mentioned otherwise.

2. Theory

We begin with writing down the MCEND wave function ansatz.

$$\Psi(\{\vec{x}_i\}, \{R_i\}, t) = \sum_{J_e}^{\text{ord}} \sum_{J_n} A_{J_e J_n}(t) |\det_{J_e}(\{\vec{x}_i\}, t)\rangle |\Phi_{J_n}(\{R_i\}, t)\rangle \quad (1)$$

with electronic position and spin degrees of freedom (dof)

$$\vec{x}_i = (\vec{r}_i, s_i), \quad i = 1, \dots, N_e \quad (2)$$

and nuclear degrees of freedom

$$R_i, \quad i = 1, \dots, 3N_n - 6(5)$$

This notation reflects the fact, that electronic and nuclear dof are usually treated in different ways. While electrons are typically described by Cartesian coordinates, nuclear dynamics is mostly done in internal coordinates, like bond lengths and angles. The number five in parentheses in Eq. (3) holds for linear molecules. To shorten the notation, we will from now on refer to the number of nuclear dof by the symbol f . More important is the difference in quantum statistics between electrons and nuclei. Correspondingly, the right-hand-side (rhs) of Eq. (1) is split into determinants \det_{J_e} and Hartree products Φ_{J_n} . Each determinant is identified by an N_e -tuple $J_e = (j_1^e, \dots, j_{N_e}^e)$ of indices of spin orbitals $\varphi_{j_k}^e(\vec{x}_k, t)$. Because of the permutational symmetry of determinants, the summation is restricted to ordered J_e , only. The $J_n = (j_1^n, \dots, j_f^n)$ are composite indices, which enumerate the single particle functions (SPFs) $\varphi_{j_k}^{n,k}(R_k, t)$ for the nuclear degrees of freedom. No specific symmetry is assumed for them, so that the summation goes over all possible combinations.

Second, we need to consider the molecular Hamiltonian. It consists of five parts,

$$H_{mol} = T_e + T_n + V_{ee} + V_{en} + V_{nn} \quad (4)$$

with the usual kinetic energies of the electrons T_e , the nuclei T_n , the electron–electron repulsion V_{ee} , the electron–nuclear attraction V_{en} , and the nuclear–nuclear repulsion V_{nn} . The derivation of the equations of motion (eom) for the coefficients, the spin orbitals for the electrons, and the SPFs for the nuclei follows the one of MCTDH and MCTDHF, which were given in detail in other Letters [2,3,9,11]. Hiding for the moment all technical difficulties, we repeat here the results in a compact notation. The eom for the coefficients is

$$\dot{A}_{J_e J_n} = -i \sum_{L_e}^{\text{ord}} \sum_{L_n} \langle \det_{J_e} \Phi_{J_n} | H_{mol} | \det_{L_e} \Phi_{L_n} \rangle A_{L_e L_n} \quad (5)$$

The eom for the spin orbitals is

$$\dot{\vec{\varphi}}^e = -i(1 - P^e)(\rho^e)^{-1} \langle H_{mol} \rangle^e \vec{\varphi} \quad (6)$$

with a projector P^e on the space spanned by the spin orbitals, the electron reduced density matrix ρ^e , and the mean fields $\langle H_{mol} \rangle^e$. Analogously, one has for the SPFs

$$\dot{\vec{\varphi}}^{n,k} = -i(1 - P^{n,k})(\rho^{n,k})^{-1} \langle H_{mol} \rangle^{n,k} \vec{\varphi}^{n,k} \quad (7)$$

with the projector $P^{n,k}$ on the space spanned by the SPFs for the k -th nuclear degree of freedom, the corresponding reduced density matrix $\rho^{n,k}$, and the mean field fields for that dof.

For the four parts of the molecular Hamiltonian T_e, T_n, V_{ee} , and V_{nn} the evaluation of these eom proceeds as reported previously for MCTDH and MCTDHF. The challenge is to evaluate the terms that involve the electron–nuclear coupling. For this, we need to introduce the primitive, time-independent bases for the orbitals

and SPFs. The electronic orbitals are expanded in a set of atom centered, Gaussian type atomic orbitals (AOs), designated as $|\mu\rangle$, and $|\nu\rangle$. We assume that they have been orthogonalized prior to any calculation [15]. The nuclear SPFs can be represented with the help of grid points or basis functions for the k th dof. Here, we choose the former, and designate them as $|\alpha_k\rangle$. With this, we can evaluate the electron–nuclear coupling term in the eom of the coefficients as

$$\left\langle \det_{J_e} \Phi_{J_n} \left| \sum_{A,i} \frac{-Z_A}{|\vec{R}_A - \vec{r}_i|} \right| \det_{L_e} \Phi_{L_n} \right\rangle \quad (8)$$

$$= \sum_{\alpha_1} \dots \sum_{\alpha_f} \Phi_{J_n}^*(\{\alpha_k\}) \Phi_{L_n}(\{\alpha_k\}) \times \left\langle \det_{J_e} \left| \sum_{A,i} \frac{-Z_A}{|\vec{R}_A(\{\alpha_k\}) - \vec{r}_i|} \right| \det_{L_e} \right\rangle \quad (9)$$

where the index A enumerates the nuclei with charges Z_A , in the molecule. For each given set $\{\alpha_k\}$ the transform to cartesian space $\vec{R}_A(\{\alpha_k\})$ is required, and the one-electron integrals

$$\left\langle \mu \left| \frac{-Z_A}{|\vec{R}_A(\{\alpha_k\}) - \vec{r}_i|} \right| \nu \right\rangle \quad (10)$$

can be calculated with standard quantum chemistry packages. It is evident, that the basis functions of the internal coordinates $\{\alpha_k\}$ should be chosen such, that they correspond to atom centers of the electronic basis set $|\mu\rangle, |\nu\rangle$. With this choice, the electronic basis does not change, when the atoms move. This is in contrast to the standard calculations of potential energy surfaces, and implies that we can thus avoid the calculation of diabatic coupling functions. This will be discussed in more detail below. The matrix elements with respect to determinants in Eq. (8) follow then from Slater–Condon rules [15].

The operator V_{en} appears also in both kinds of mean fields. The latter are defined through single hole functions. For the electrons these are given by:

$$\Psi_j^e = \sum_{J_{\text{SHD}}}^{\text{ord}} \sum_{J_n} A_{j J_{\text{SHD}} J_n} \det_{J_{\text{SHD}}} \Phi_{J_n} \quad (11)$$

The first summation in Eq. (11) is over all single hole determinants (SHD), i.e. all determinants with $N_e - 1$ electrons.

The electronic mean fields are single particle operators, with matrix elements

$$\langle \mu | \langle H_{mol} \rangle_{j|} | \nu \rangle = \langle \Psi_j^e \mu | H_{mol} | \Psi_j^e \nu \rangle \quad (12)$$

Again, it is here only necessary to consider the term due to V_{en} , because the others have already been discussed elsewhere. Thus, we have to evaluate

$$\left\langle \det_{J_{\text{SHD}}} \Phi_{J_n} \mu \left| \sum_{A,i} \frac{-Z_A}{|\vec{R}_A - \vec{r}_i|} \right| \det_{L_{\text{SHD}}} \Phi_{L_n} \nu \right\rangle \quad (13)$$

$$= \sum_{\alpha_1} \dots \sum_{\alpha_f} \Phi_{J_n}^*(\{\alpha_k\}) \Phi_{L_n}(\{\alpha_k\}) \times \left\langle \mu \left| \sum_A \frac{-Z_A}{|\vec{R}_A(\{\alpha_k\}) - \vec{r}_1|} \right| \nu \right\rangle \delta_{J_{\text{SHD}}, L_{\text{SHD}}} + \dots \quad (14)$$

At the center of this expression we find the same one-electron integrals that appeared already in Eq. (10). The previous comments about the matching condition of the $\vec{R}_A(\{\alpha_k\})$ and the atom centers of the AOs applies here, too. In the second line we split the terms into those involving only electron number one, and all others, indicated by the three dots. (This refers to the summation over i in Eq. (13).) The reason for this is, that all the other terms would be annihilated by the projector P^e in Eq. (6), and therefore need not be evaluated. It is a further consequence of this splitting, that the

Kronecker $\delta_{J_{\text{SHD}}, L_{\text{SHD}}}$ appears in Eq. (14), which simplifies calculations greatly. With this, the new term in the electronic mean fields can be evaluated as

$$\begin{aligned} \langle \Psi_j^e | \mu | V_{en} | \Psi_l^e \rangle &= \sum_{J_{\text{SHD}}}^{\text{ord}} \sum_{J_n} \sum_{L_n} A_{(J_{\text{SHD}})J_n}^* A_{(J_{\text{SHD}})L_n} \\ &\times \sum_{\{\alpha_k\}} \Phi_{J_n}^*(\{\alpha_k\}) \Phi_{L_n}(\{\alpha_k\}) \left\langle \mu \left| \sum_A \frac{-Z_A}{|\vec{R}_A(\{\alpha_k\}) - \vec{r}_1|} \right| v \right\rangle \end{aligned} \quad (15)$$

The calculation of the nuclear mean fields follows this derivation above closely, and is therefore not given here explicitly.

3. Illustrative calculations

In this section we present some illustrative calculations to show how the method works. As an example we choose a LiH molecule, which has $N_e = 4$ electrons and $f = 1$ nuclear degrees of freedom. For the electrons, we have chosen the STO-3G basis set, and a grid of 38 grid points along the bond length R . In order to solve the equations of motion, the matrix elements of Eq. (10) have to be calculated. Four distances with $R_1 = 1.512a_0$, $R_2 = 3.024a_0$, $R_3 = 5.291a_0$, and $R_4 = 7.559a_0$ (corresponding to $R_1 = 0.8 \text{ \AA}$, $R_2 = 1.6 \text{ \AA}$, $R_3 = 2.8 \text{ \AA}$, and $R_4 = 4.0 \text{ \AA}$) have been chosen. The center of mass has been held fixed, in order to facilitate the transform from R to R_{Li} and R_H , the actual positions of the atoms in real space. Because we make the requirement, that the electronic basis set must not change with the nuclear positions, it is necessary to place the same basis functions at the positions of ‘ghost atoms’, for those distances that are different from the actual bond length, for each evaluation of Eq. (10). This is illustrated in Fig. 1. The combined basis set consists of functions at each of the four ‘sampling’ positions of the atoms. The basis functions are indicated by Gaussians, at the correct distances given above, but with only representative widths. One STO-3G basis set for LiH contains six atomic orbitals, so that because of the four positions Eq. (10) defines a 24 by 24 matrix. It is this setup, that enables us to avoid the calculation of kinetic couplings, or Pulay forces. But Fig. 1 also illustrates a problem: The overlap between the Gaussians is considerable, leading, in general, to linear dependencies [15]. This is measured by the smallest eigenvalue of the overlap matrix $S_{\mu\nu} = \langle \mu | \nu \rangle$. In the present case, this was 1.4×10^{-7} , which is smaller than what most quantum chemistry packages would accept for HF or other calculations, but in the present context is just manageable. If larger basis sets shall be used, it will be necessary to remove these (almost) linear dependencies first. Evidently, the use of an even denser combined basis set would be much more complicated. It is therefore fortu-

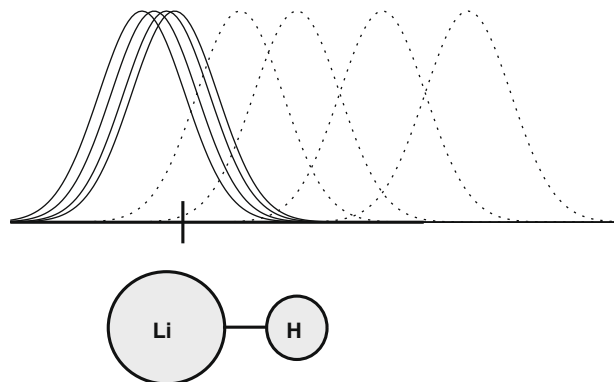


Fig. 1. Sketch of the basis functions. The position of the Gaussians (solid lines for Li, dotted lines for H) is drawn up to scale, for four different bond lengths. The width of them is just representative of the functions in the STO-3G basis set.

nate, that only a potential energy term which varies slowly with the bond length, has to be treated this way. The matrix elements of the other 34 grid points in R can thus be obtained by spline interpolation.

We will now turn to the determination of the correlated ground state of the molecule by propagation in imaginary time (PIT). We have chosen this example for three reasons. First, because this will provide information about the electron–nuclear correlation, through the energy difference for various expansion lengths. Second, in order to perform a real time simulation, it is necessary to know the ground state as the initial state. And third, PIT involves the solution of the equations of motion, and is thus a first example of their application.

Also for PIT, an initial state has to be chosen. The electronic orbitals have been initialized by a core guess at the position close to the expected equilibrium bond length R_2 . For the calculations with only a single SPF, its initialization was done as follows: From HF calculations at the four positions we obtain a first guess for the ground state potential energy surface. The four HF energies, together with a cubic polynomial through these points is shown in Fig. 2. By diagonalization we obtained the vibrational ground state, which served as initial condition for the PIT.

In the following we will denote the various expansion lengths of the MCEND wave function by $(n_e/2, n_n)$, where n_e is the number of spin orbitals, and n_n is the number of SPFs for the nuclear degree of freedom. Fig. 3 shows the energy expectation value as a function of imaginary time. We will focus on the $n_n = 1$ cases, first. At initialization, the energy is quite high, because the core guess does not have much overlap with the actual ground state. After about 5 fs the total energies have converged. However, an inspection of the nuclear position and kinetic energy expectation values shows, that the wave functions are still changing (not shown). Going from (2, 1) to (4, 1), i.e. from a single to 70 determinants, 0.668 eV correlation energy is gained. We know from MCTDHF calculations, that this is around 85% of the total correlation energy. When using $n_n = 2$ SPFs, we found that the propagations were quite unstable. The reason is probably, that the ca. 30 eV that have to be removed by the PIT (it starts at -182.7 eV , and is extremely steep at the beginning), is too much for the vibrational degrees of freedom. Therefore, we have taken the final state of the $(n_e, 1)$ PITs, and obtained the second SPF by multiplication with the momentum operator and successive orthogonalization. The resulting energy expectations values for these PITs is also shown in Fig. 3, as thin dashed and dotted lines. Again, while the total energies relax very fast, the wave

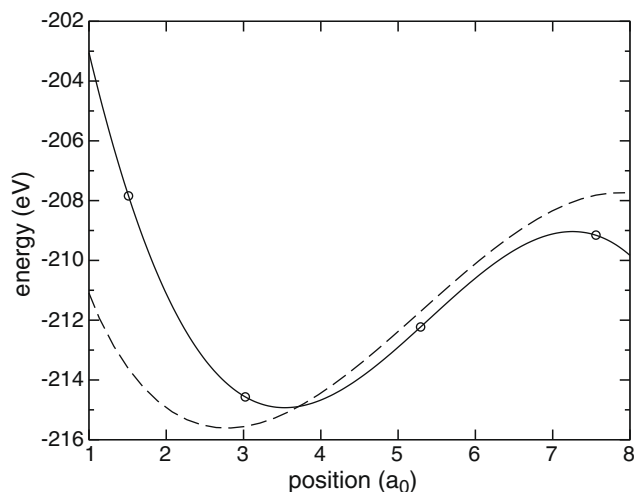


Fig. 2. Approximate potential energy surfaces. The circles correspond to the HF energies at various bond length, the solid line is a cubic spline to these points, and the dashed line is inferred from the ground state SPF of the (4, 1) calculation.

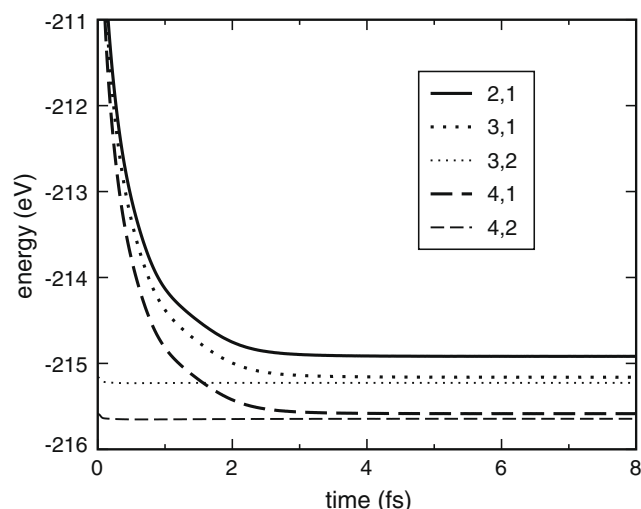


Fig. 3. Propagation in imaginary time. The energy expectation value approaches the ground state energy for various MCEND expansion lengths. For details see text.

functions require the full 8 fs. In the case of (3,2) the energy is lowered by 2.4 meV, while in the case of (4,2) the energy is lowered by 2.2 meV. This is evidence for a weak but non-zero correlation between the electronic and nuclear degrees of freedom.

Finally, one may ask, by what potential the nuclei ‘feel’ due to the electrons. This is the search for a Born–Oppenheimer separation in a correlated calculation. If only a single SPF is used, we can construct an effective nuclear Hamiltonian $H_n = T_n + V_n$ by shifting the ground state energy up to zero, and requiring

$$H_n \varphi_1^n = 0 \quad (16)$$

which leads to the definition of an effective potential

$$V_n(R) = \frac{-T_n \varphi_1^n(R)}{\varphi_1^n(R)} \quad (17)$$

This $V_n(R)$ for the final state of the (4,1) PIT is shown as dashed line in Fig. 2. Surprisingly, it shows a shorter equilibrium bond length than the HF potential, which we attribute to the small basis set in our calculations. For the same reason, we do not compare these results to experimental values at this state of development. If more than one SPF is used, the nuclear ground state is determined by a density matrix. A potential that is deduced from the condition $[H_n, \rho_n(R, R')] = 0$ would be a non-local one, $V_n(R, R')$, for the same reason that leads to a non-local effective HF potential. However, in the (4,2) calculation the natural population of the second SPF was not more than 1.076×10^{-3} , so that the resultant potential would be almost local, and identical to the one shown in Fig. 2.

4. Summary and outlook

The multi-configuration electron–nuclear dynamics method presented in this Letter describes an approach to fully quantum,

correlated, ab initio, and non-adiabatic dynamics. The calculation of potential energy surfaces and kinetic couplings is avoided, as well as the appearance of Pulay forces. It is clearly a computationally expensive method. The two largest calculations, MCEND (4,1) and (4,2), took 3 h and 12 h respectively on a modern PC. This limits the applicability to small molecules. The preceding section has illustrated how these calculations can be performed, and that the fully correlated molecular ground state can be obtained, which is the starting point for dynamics in real time. The 12 + 1 dimensional LiH system is, to our knowledge, the largest one for which such kind of simulation has been attempted. Future calculations will need to remove linear dependencies from the set of GTOs. Algorithms for this are already available in the literature [15]. Also, this method requires very little memory, but a large amount of CPU time, making it well suited for shared memory parallelization.

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