



Electron dynamics across molecular wires: A time-dependent configuration interaction study



Raghunathan Ramakrishnan*, Shampa Raghunathan, Mathias Nest

Theoretische Chemie, TU München, Lichtenbergstr. 4, 85747 Garching, Germany

ARTICLE INFO

Article history:

Received 5 February 2013

In final form 4 May 2013

Available online 14 May 2013

Keywords:

Electron dynamics

Core-hole

Many electron correlation

Configuration interaction

Electron trapping

ABSTRACT

In this study we present methodological developments of the time-dependent configuration interaction (TDCI) method for ab initio electron dynamics in donor–bridge–acceptor systems. Especially, we investigate the role of valence electron correlation, the scheme for selecting the determinantal basis, and the computational effort. Our test systems are molecules of the type $\text{Li}-(\text{C}_2)_n\text{-CN}$, $\text{Li}-(\text{C}_2\text{H}_2)_n\text{-CN}$, and $\text{Na}_9-(\text{C}_2\text{H}_2)_2\text{-CN}$. In this way, this study is intended as a step towards rigorous description of charge transfer in molecular wires attached to metal surfaces or nanoparticles using a many-electron wavefunction. Also, a multi-reference configuration interaction singles approach is suggested as a good compromise between computational effort and accuracy.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Ab initio electron dynamics has by now almost as many methods available as standard electronic structure theory. The methods of the latter have been generalized to the real time domain, and their properties have been explored. The earliest approaches were time-dependent Hartree–Fock (TDHF) [1] and TD density functional theory (TDDFT) [2]. Although they have had some successes [3–6], it has increasingly been found that their accuracy is hard to predict [7–11]. The extension of complete active space self-consistent field (CASSCF) yielded the multi-configuration time-dependent Hartree–Fock (MCTDHF) [12,13] method. The time-dependent orbitals make MCTDHF a very flexible method, which can also describe high-energy processes, like ionization, but the requirement of making a four-index integral transform in each time-step also renders it applicable to only small systems. At present there are two ab initio methods, that can treat larger systems at least qualitatively correctly. One is the algebraic diagrammatic construction scheme by Kuleff et al. [14] and Dutoi and Cederbaum [15], the other is time-dependent configuration interaction (TDCI) [16–19]. The TDCI approach is conceptually very simple, however, TDCI also requires a set of determinants to be chosen as many-body basis functions. On the one hand, selecting only single excitations (TDCIS), has often been enough for proof of concept calculations [17,20,21]. On the other hand, it is well known that double excitations (TDCISD) are important to describe many-body correla-

tion and electron–electron scattering [18]. Yet, an all-electron correlated TDCISD is often already too expensive computationally, to be applied to large systems. These two schemes, which are common in ground state calculations, are therefore not optimal for time-dependent studies. This is the starting point for this paper. For the example of intramolecular charge transfer we will show, that a multi-reference CIS selection of determinants gives qualitatively correct results, and that comparatively large systems can be treated, when additionally parallelization and sparse matrix techniques are used. Naturally, all CI based methods (except full CI) will suffer from the lack of size-consistency, but this should not prevent efforts to develop TDCI further. Especially, it should be avoided to select the doubly excited determinants by hand, according to chemical intuition for example, because this can lead to a significant bias. In addition, the calculations shown here are intended as a first step towards an ab initio description of charge transfer through a molecular wire to metal surfaces. Here the initial state is already a wave packet composed of excited determinants only, so that the problem of too high excitation energies, from which CISD usually suffers, is avoided. This will be discussed in detail below. All calculations are done in the fixed-nuclei approximation, which is valid on the ultrashort time scales involved.

The systems we are looking at are molecular wires, with a cyanide group at one end, which serves as a chromophore or an electron donor group. Molecular wires have been studied extensively before: Either by looking at current–voltage characteristics [22–25], or ring currents [26–28], or electronic wave packets [14,16,29–31]. This special setup, which we are studying here, has been used in recent experiments by Feulner and coworkers [32–36]. There, cyanide terminated molecules, prepared as self-

* Corresponding author.

E-mail address: rama@mytum.de (R. Ramakrishnan).

assembled monolayers on a gold surface, were excited using synchrotron radiation, and the charge transfer to the surface is measured by the core-hole clock (CHC) method. The CHC method involves the detection of Auger electrons, which can not be simulated with the present TDCI methodology. Both the problem of basis sets and the difficulty to treat core correlation accurately prevent this. However, it is our long-term objective to simulate the charge transfer measured with the CHC, even in the absence of ionization. But before that can be done, a significant amount of methodological development is necessary. Apart from the question of the optimal selection of the determinantal basis, we will (i) look into time-dependent Mulliken and Löwdin charges as a tool to describe the dynamics, (ii) study the role of valence correlation in the initial state, and (iii) see whether small metal clusters are suitable to capture an electron, after it is excited at an adsorbed molecule. The experimentalists identified the initial state of the charge transfer process as an excitation from the nitrogen 1s core orbital of CN to one of two unoccupied π^* orbitals. At present, we do not aim at a simulation of the excitation process itself, but take their assignment as granted, and only support it with arguments based on oscillator strengths. In the experiment, the π^* orbital is energetically above the conduction band of the metal, so that the electron is transferred into the bulk. Before proceeding to describe this process accurately, it is necessary to explore which level of theory is required, and whether larger and more complex systems are tractable at all. To this end, we have replaced the gold surface with a lithium atom or a sodium cluster.

The following sections of this paper will discuss the requirements for simulations as described above, with a special emphasis on the determinantal basis, role of valence electron correlation, and computational effort. Also, we analyze the dynamics of the excited electronic wave packet for various molecules.

2. Computational details

2.1. Geometry and integrals

In this study we are treating electron dynamics in the seven molecules LiCN, Li-(C₂)_n-CN and Li-(C₂H₂)_n-CN, where $n = 1, 2, 3$, and the molecule-metal cluster system Na₉-(C₂H₂)₂-CN. The equilibrium geometries of all molecules are computed at the Hartree-Fock (HF) level by employing the 6-31G* [37,38] basis set for the atoms H, Li, C, N and an effective core potential (ECP) with the CEP-4G basis set [39] for the Na atom. These Gaussian Type Orbital basis sets can not describe electrons far from the nuclei, so they effectively place the system in a box. But the dynamics we are interested in involves only molecular orbitals slightly above the HOMO (highest occupied molecular orbital), so that this is not a severe restriction. The geometry optimizations were performed without enforcing any symmetry constraints using the program packages PSI3 [40] and Gamess [41]. Because the former program does not employ ECPs, the calculation of Na₉-(C₂H₂)₂-CN was performed using the program Gamess. One- and two-electron integrals and the HF ground state molecular orbitals (MOs) required for the TDCI computation are obtained using an interface to PSI3 and Gamess.

2.2. Analysis

For the TDCI calculations described in the following section we have used the direct TDCI method, i.e., the wave function and the Hamilton operator were represented in the basis of the Slater determinants, and also the propagation is done in the same representation. In this way we avoid the intermediate step of calculating the electronic eigenvalues and eigenstates of the molecule, which

would be too costly for the systems we are interested in. Our procedure to select the determinants which enter the many-body basis set will be described below. Our main tool to analyze the dynamics are the Mulliken charges

$$q_A(t) = Z_i - \sum_{\mu \in A} (\mathbf{P}(t)\mathbf{S})_{\mu\mu}, \quad (1)$$

where \mathbf{S} is the atomic orbital overlap matrix, and $\mathbf{P}(t)$ the reduced density matrix, which we compute from the many-body wave function on the fly. We have chosen this quantity to describe the motion of the electronic wave packet, because it provides a more detailed picture, compared to simple observables like the position expectation value or the dipole moment. Also, in the future there might be the possibility to spatially resolve the motion of an electronic wave packet inside a molecule, and then the atomic charges provide additional useful information. However, one has to be aware that in a time-dependent context $\mathbf{P}(t)$ is complex, so that the Mulliken charges acquire an imaginary part. We report only real parts in the following, alternatively, one can rederive Mulliken's formula for complex density matrices [42]. This yields strictly real populations, which are identical to the real parts of the Mulliken charges using the original formula. As a second alternative, one can also use the Löwdin charges

$$q_A^L(t) = Z_i - \sum_{\mu \in A} (\mathbf{S}^{1/2}\mathbf{P}(t)\mathbf{S}^{1/2})_{\mu\mu}, \quad (2)$$

which are always real. Other definitions for atomic charges are available, like Bader atomic charges [43], but they all suffer from the arbitrariness of assigning a part of the electronic cloud to one atom. Nevertheless, in most applications they provide qualitatively correct results especially when looking at the relative charges, i.e. $q_A(t) - q_A(0)$. We provide one comparison of the Mulliken and Löwdin definitions at the end of the paper, which also helps to estimate the effect of different definitions.

2.3. Initial state

The initial excited state of interest here is formed by the excitation of an electron from the N 1s to a π^* orbital which is formally localized on the CN group. To translate this seemingly simple description into a CI wave function is however quite difficult. If the molecule were in its Hartree-Fock ground state Ψ_{HF} , then this single excitation could be described trivially with a single excited determinant $\Psi_{N1s}^{\pi^*}$. But suppose, we are dealing with a CISD wave function:

$$\Psi = C_0\Psi_{HF} + \sum_S C_S\Psi_S + \sum_D C_D\Psi_D, \quad (3)$$

in the correlated ground state no coefficient is identically 1, and almost all are non-zero. The correlation of the electrons is encoded in the C_D coefficients. In practice, one has two possibilities: Either we ignore correlation altogether, and simply set the coefficient of $\Psi_{N1s}^{\pi^*}$ to one, and that of the HF ground state to zero. Or, we start from the correlated ground state, and swap the coefficients of the HF ground state, and the singly excited target state. In this way, the correlation of the valence electrons is preserved. We will discuss both possibilities in the next section. Please note that this procedure for the construction of the initial state avoids the problem of a relatively high ground state correlation of TDCISD, because the exact excitation energy does not appear.

2.4. Selection of determinants

As pointed out in the introduction, it is necessary to select the determinants which enter the expansion of the wave function prior

Download English Version:

<https://daneshyari.com/en/article/5373929>

Download Persian Version:

<https://daneshyari.com/article/5373929>

[Daneshyari.com](https://daneshyari.com)