Time-dependent restricted active space Configuration Interaction theory applied to the photoionization of neon

David Hochstuhl and Michael Bonitz
Institut für Theoretische Physik und Astrophysik, D-24098 Kiel, Germany
E-mail: hochstuhl@theo-physik.uni-kiel.de

Abstract. We give a presentation on the time-dependent restricted active space Configuration Interaction method, which has been recently introduced [D. Hochstuhl, M. Bonitz, PRA, in press] to efficiently tackle the few-particle nonequilibrium many-body problem. Particularly, we apply it to the calculation of photoionization cross sections and angular resolved ionization yields of groundstate neon.

1. Introduction
The rapidly increasing quality of experimental techniques in the generation of sub-femtosecond laser pulses has led to a lot of new insights and surprises. For example, in a recently performed experiment using the attosecond streak camera, i.e. a combination of attosecond extreme ultraviolet (XUV) pump and infrared (IR) probe spectroscopy, a time-delay in the photoemission of electrons from the 2s and 2p-shells of neon has been observed, with the 2s-electron leaving the neon atom around 21 attoseconds before the 2p-electron [1]. Similar results have been also obtained using different attosecond techniques for the argon atom [2]. Another recent combined experimental and theoretical study considering as well XUV pump pulses but terahertz pulses for the probe revealed the existence of a chirp in the emission of Auger electrons [3, 4].

A general framework for the theoretical description of such explicitly time-dependent photoionization processes is given by the time-dependent Schrödinger equation (TDSE) which, due to the lack of analytical solutions, must be tackled through computer simulations. For one- and two-particle systems, the numerical approach is nowadays routinely applied, as can be observed by a plethora of investigations on helium and atomic and molecular hydrogen. For larger electron numbers, however, direct numerical solutions are unfeasible for all but very small grid sizes, which is a direct consequence of the exponentially growing effort required to store and process the discretized wavefunction. This fact is well known in computer science under the name exponential wall or the course of dimensionality, and beside the Schrödinger equation does affect several other disciplines such as combinatorics, optimal control or graph theory.

The basic problem can be readily illustrated: consider the $N$-particle fermionic wavefunction $\Psi(x_1,\cdots,x_N,t)$, where $x_k$ is a complete observable of electron $k$ at time $t$, and assume that the state $x_k$ is described by a number of $N_k$ attributes, the basis functions. Then, a general wavefunction would have to assign a complex number to each of the $\binom{N_k}{N}$ possible ordered combinations of $(x_1,\cdots,x_N)$. The accurate simulation of photoionization applications now can
easily require basis sizes of $N_b \sim 10000$, as the electrons may travel to large distances from the ionic nucleus, so that the corresponding wavefunction becomes too difficult to manage in numerical calculations. The same is true for the case of a moderate basis size but a large number of particles, as it is encountered, for instance, in quantum chemistry.

Several workarounds have been designed to avoid this fundamental issue. Multiconfigurational time-dependent Hartee-Fock theory, for instance, uses a smaller single-particle basis which are time-dependent, and in this way tries to reduce the determinant size [5–7]. Time-dependent density-functional theory (TDDFT) replaces the wavefunction by the single-particle density $\rho(x,t)$, i.e. by a much reduced quantity. Density-matrix functional theories instead employ the generalized one-particle density $\rho(x,x',t)$, whereas nonequilibrium Greens functions (NEGFs) $G(xt,x't')$ even keep the information of a second time variable, which is basically related to the system’s ionization energies and electron affinities. The exact equations of motion for these kind of approximations usually involve a coupling to higher order density matrices or Greens functions, which, in order to obtain a closed scheme, must be approximated in terms of the respective reduced quantity. Depending on the contained information, this reconstruction can be performed more (NEGFs) or less (TDDFT) systematically. In any case, the error of the result can hardly be controlled.

The time-dependent restricted active space Configuration Interaction (TD-RASCI) method presented in this work follows a different approach, which is set completely on the $N$-particle level. In order to reduce the exponential problem, the domain of the wavefunction is restricted. In the above mentioned example, one could for instance allow only one electron to travel to large distances from the core, whereas the remaining $(N-1)$ particles are restricted to a narrow region in the vicinity of the nucleus. Given that the $(N-1)$ particles can be described by a reduced number of basisfunctions of say $N_b \sim 100$, the discretized domain $(x_1, \cdots, x_N)$ becomes smaller by roughly a factor of $100^{N-1}$ as compared to the previous example using 10000 basisfunctions for all particles. This enables the treatment of systems having a much larger number of particles.

In the following, we summarize the TD-RASCI method, which has been proposed in our former work [8]. Thereafter, in section 3, we apply the method to the calculation of angular resolved photoionization cross sections and asymmetry parameters of the Neon atom.

2. TD-RASCI method

The time-dependent restricted active space Configuration Interaction method begins with an ansatz to the $N$-particle wavefunction in terms of Slater determinants,

$$\begin{align*}
|\Psi(t)\rangle = \sum_{I \in \Omega} C_I(t) \left| \psi_{i_1} \psi_{i_2} \cdots \psi_{i_N} \right>. 
\end{align*}$$

(1)

where the multi-index $I = (i_1, \cdots, i_N) \in \Omega$ specifies the occupied single-particle spin-orbitals $| \psi_k \rangle$. The included Slater determinants are determined by the index set $\Omega \subset \mathbb{N}^N$. By choosing all anti-symmetrized indices which are possible for $N$-particles and $N_b$ orbitals,

$$\Omega = \{(i_1, \cdots, i_N) | 1 \leq i_1 < \cdots < i_N \leq N_b\},$$

(2)

one obtains the Full Configuration Interaction (FCI) ansatz: the wavefunction is completely correlated and exact up to the finite size of the spin-orbital basis. In many cases, however, the FCI expansion is unnecessary complex as a large number of Slater determinants never get occupied during the propagation. The idea of the TD-RASCI scheme is therefore to drop those determinants from the expansion which are considered to be of minor importance. The selection procedure must thereby be performed in advance, i.e. one should at best be aware of the physical processes that are expected to occur and then try to incorporate these processes in a way that the calculation becomes manageable.
In practice, the selection can hardly be performed manually, but rather a systematic procedure should be applied. Such one is presented in our former work [8]. Thereby, the single-particle basis space is first divided into a chosen number of partitions, and then restrictions are imposed onto the occupation of these partitions. To take up the example of the introduction, for the calculation of single-electron photoionization it is convenient to divide the coordinate space into an inner bound region and outer continuum region and allow for at most a single electron in the outer region. The corresponding wavefunction is then given by

\[ \Psi(t) = \sum_{I \in \Omega} \sum_{j=1}^{N_b} C_{I,j}(t) \hat{A} |\phi_i \cdots \phi_{i_{N-1}}\rangle |\phi_j\rangle, \]  

(3)

which is set up in terms of a localized basis set \{ |\phi_k\rangle \}, of which some basis functions are located only in the inner region and others only in the outer region. The index set \( \Omega_{N-1} \) then is taken to include only indices corresponding to inner basis functions, while the second sum runs over the whole orbital basis. The total size of the wavefunction expansion (3) is given by \( N_{\text{det}} = N_b|\Omega_{N-1}| \) and requires therefore, at least for small cardinality of \( \Omega_{N-1} \), a similar effort than a single-particle problem. In case \( \Omega_{N-1} \) contains only a single \((N-1)\)-particle determinant, one recovers the single-active electron approximation. Note, however, that in contrast to the commonly employed SAE approaches the inter-shell interaction is treated in a consistent way and no pseudo-potentials are required whatsoever. It is further straightforward to consider more sophisticated approximations, e.g., allowing for two electrons outside, or even for more elaborate choices. Using a reasonable computer implementation, such as the one presented in Ref. [8], this is accomplished simply by a change of the input parameters.

For the present work, we consider only single ionization and therefore apply the wavefunction expansion given in Eq. (3). The single-particle basis set is given by

\[ \phi_{klm\sigma}(r, m_s) = \frac{\chi_k(r)}{r} Y_{lm}(\theta, \phi) \sigma(m_s), \]  

(4)

where \( Y_{lm} \) denote spherical harmonics, \( \sigma \) the spin function \((\sigma \in \alpha, \beta)\), and the radial functions \( \chi_k \) are taken to be finite-element discrete variable representation (FEDVR) functions [9]. In short, a FEDVR constitutes a basis of Lagrange interpolating polynomials constructed over a Gauss-Lobatto grid, which on the one hand is flexible in describing arbitrary functions, and on the other leads to a sparse representation of the electron integrals. If we now applied the basis (4), we would observe that a large number of determinants were required in the inner region to obtain an appropriate initial state, which is caused by the fact that Lagrange polynomials do not resemble atomic orbitals. Hartree-Fock orbitals, on the other hand, provide a reasonable initial state with a few determinants, but have the disadvantage that the electron integrals are not sparse at all, which poses a severe restriction on the applicable size of the basis. The solution is to use a mixed basis of Hartree-Fock and FEDVR functions, where the Hartree-Fock problem is solved in the first finite element using the FEDVR basis, and the thus obtained eigenfunctions replace the FEDVR functions in the first element. The arising basis set is illustrated in Fig. 1. The mixed basis has the advantage that it provides an appropriate initial state in the region near the nucleus, while in the continuum it exploits all the advantages of a grid-like treatment. Note that, due to the unitary transformation in the first element, no reflections or similar problems arise at the element boundary.

Having constructed an appropriate TD-RASCI ansatz, the further steps are straightforwardly similar to any direct approach such as Full Configuration Interaction. Insertion of the ansatz into the time-dependent Schrödinger equation leads to the equation of motion for the expansion
Figure 1. Mixed basis applied in the TD-RASCI method for the efficient treatment of photoionization. It consists of a Hartree-Fock basis in the region near the atomic core and a finite-element discrete variable representation in the region outside \( r = 20 \) bohr, the continuum. The mixed basis, on the one hand, provides an appropriate initial state which is set up by a small number of determinants and, on the other, exploits the advantages of the grid-like treatment in the continuum.

coefficients,

\[
i \dot{C}_I(t) = \sum_{J \in \Omega} \langle \phi_{i1} \cdots \phi_{iN} | \hat{H}(t) | \phi_{j1} \cdots \phi_{jN} \rangle C_J(t),
\]

where we apply a Hamiltonian of the form

\[
\hat{H}(t) = \sum_{k=1}^{N} \left\{ \frac{p_k^2}{2} - \frac{Z}{r_k} + E(t) \cdot r_k \right\} + \frac{1}{2} \sum_{k \neq l} \frac{1}{|r_k - r_l|},
\]

which consists of kinetic and potential energy, the Coulomb interaction and the action of an electromagnetic field coupled in dipole approximation. The arising Hamiltonian matrix elements between Slater determinants are evaluated using Slater-Condon rules [10] and stored in sparse matrices. The initial state is found using the Lanczos method which iteratively constructs the groundstate using only matrix-vector products, and the thus obtained groundstate is then propagated with the time-dependent version of the Lanczos method [11]. At the end of the propagation, we use the ionized part of the wavefunction [the factor \(|\phi_j\rangle\) in Eq. (3)] to extract the relevant information of the ionized particle.

3. Single-photoionization of Neon

Neon is a common target in photoionization studies, which has been investigated several times in the previous half century. Theoretically, its closed-shell structure facilitates the application of theoretical methods, and several methods such as perturbation theory [12], Hartree-Fock [13] or random-phase methods [14], R-matrix theory [15] or the Stieltjes-Chebyshev moment technique [16] have been used to calculate cross sections. Furthermore, experimentally measured cross sections can be found in Refs. [17–19]. In this work, we calculate total and
Figure 2. Ionization yield plotted versus time for photoionization from the groundstate of neon subjected to the laser field shown in the top panel. The photon energy is 25 eV and the intensity is $10^{12}$ W/cm$^2$. The TD-RASCI method predicts a slightly larger ionization yield than the (3s) and (3s,3p) approximations (see text).

angular-resolved photoionization yields with the TD-RASCI method. The basic form of the wavefunction is given in Eq. (3), i.e. we consider single-ionization, where only one particle is allowed in the continuum (outside $r > 20$ bohr). For the wavefunction in the inner region, which is determined by the set $\Omega_{N-1}$, we consider three approximations: (i) the TD-CIS approximation where only the Hartree-Fock groundstate plus all single-excitations is included, (ii) the approximation where double-excitations up to the 3s orbital are allowed which is denoted (3s) in the following, and (iii) the approximation where double-excitations to the 3s orbital and further to the 3p orbitals are allowed [denoted (3s, 3p)]. The single-particle basis we use consists of partial waves up to $l = 3$ and a radial grid that extends up to 400 bohr and consists of finite elements of length 4 bohr which include 10 basisfunctions each (except for the first one which includes 20 basisfunctions). The total number of Slater determinants used to describe the wavefunction is 32447 for the TD-CIS approximation, 237922 for the (3s) approximation, and 454151 for the (3s,3p) approximation. The neon atom is propagated for $T = 200$ a.u. under the action of an laser pulse with a sine-squared envelope (also with duration $T$). The calculations take in between 90 minutes on a single processor for the TD-CIS approximation and 48 hours for the (3s,3p) approximation.

Figure 2 depicts the ionization dynamics for photoionization from the neon groundstate with the 25 eV pulse shown in the top panel. A particle is thereby considered as being ionized if it is located outside a radius of 20 bohr from the nucleus. All three TD-RASCI approximations show the same qualitative behavior: a steep rise around $t = 100$ a.u., which is delayed with respect to the field due to the time needed to travel to $r = 20$ bohr, followed by a saturation around the end of the pulse. The TD-CIS approximation produces the largest yield and a slightly earlier
For a laser pulse with duration 200 a.u. and an intensity of \(10^{12}\) W/cm\(^2\).

All three approximations produce cross sections which rise around the Hartree-Fock ionization energy which is 23.15 eV for Neon. One further obtains a monotonic decrease towards larger photon energies. Around 50 eV, we observe the 2s\(2p^6\) 3s resonance, the exact location of which is 45.547 eV according to the NIST database. The better approximations shift the position of the resonance towards the wrong direction. When comparing the calculated cross section to experimental results, we further observe that the calculations are 10\% larger than the measured values in Ref. [19]. This reason for this discrepancy remains a subject of further investigation, since the TD-RASCI scheme usually performs well in estimating the cross sections [8].

The momentum distribution of the ionized particle for a photon energy of 70 eV is depicted in Fig. 4. The momentum is calculated through a Fourier transform of the ionized part of the wavefunction (\(r > 20\) bohr). The left picture shows the two-dimensional momentum distribution which arises from the (3s, 3p) approximation. Due to the linear polarization of the laser it is symmetric with respect to rotations around the \(z\)-axis. One clearly notices two rings which correspond to ionization from the 2s and 2p shells. The inner ring around 30 eV

**Figure 3.** Total single-photoionization cross section of neon plotted against the photon energy for photoionization from the groundstate. The duration of the laser field’s squared-sine envelope is \(T = 200\) a.u. and the intensity is \(10^{12}\) W/cm\(^2\).
Figure 4. Momentum distribution of the ionized particle for a photon energy of 70 eV. Left: Momentum distribution for the \((3s, 3p)\) approximation. One clearly notices two rings which correspond to ionization from the 2s-orbital (inner ring) and the 2p-orbital (outer ring). Right: Momentum distribution in forward direction for the three TD-RASCI approximations. The peaks which correspond to ionization from the 2s shell are multiplied by a factor of 10.

exhibits \(p\)-symmetry and stems from the ionization from the 2s-orbital. The outer ring at 50 eV corresponds to the ionization from the 2p orbitals and is dominantly of \(d\)-symmetry, but also has a contribution of \(s\)-symmetry, as can be seen since the distribution does not go down to zero, but remains at a finite value. The right panel shows the momenta from the three approximations in forward direction along the z-axis, i.e. \(\theta = 0\). It is directly obvious that the accuracy of the wavefunction has a distinct impact on the spectra. The TD-CIS results yield the highest photoelectron momentum. With increasing accuracy, both peaks shift towards a lower momentum. Interestingly, the 2s-peak shows a larger relative shift than the peak corresponding to the 2p ionization. This is likely to have a major impact in the calculation of time-delays using the streak camera principle, and indicates the importance of applying a correlated description.

4. Conclusion

In this proceeding paper, we applied the recently introduced time-dependent restricted active space Configuration Interaction method to the photoionization of the neon atom. After a recapitulation of the method, we have calculated the total cross sections for three different TD-RASCI approximations, and further considered the time-resolved photoionization at 25 eV as well as the momentum distribution at 70 eV. Particularly the momentum distribution is significantly affected by the increased amount of correlation present in the more accurate TD-RASCI wavefunctions. We therefore expect correlations to be of similar importance for the topic we plan to consider in the future, namely the calculation of time-delays in the photoionization of neon.
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