Chapter 4

Results I: Electron dynamics from TDHF theory

In this chapter we apply the TDHF method previously developed by us to realistic systems: Na$_4$, Na$_9^+$, and Pt$_3$ clusters. The small number of electrons, the simple electronic structure, the similarity to the homogeneous electron gas make the first two clusters accessible to a large variety of methods. Both static and dynamical calculations were reported in the literature. Na clusters can also easily be produced in experiment. Important information that can be measured is the optical absorption spectrum. This quantity characterizes the excitation spectrum of the system. In small metallic clusters collective excitations are very pronounced. Depending on the geometry of the clusters the plasmon peak can have a regular shape (single peak) or can split because of the absence of axial symmetry. Besides the position of the plasmon resonance we are interested in its broadening due to electron-electron interaction. It contains important information about the dynamics and relaxation processes in the system.

The situation with the Pt$_3$ cluster is much more complicated. Because of the strongly localized $d$-electrons and the complicated electronic structure this system differs very much from the jellium model. Due to the incomplete $d$-shell, and, as a consequence, the high density of states close to the Fermi level, electron-electron scattering is very important for the relaxation. It reduces the plasmon life-time from 200 fs in the closed shell transition metals to 70 fs in Pt.

The structure of this chapter is as follows. First we apply the TDHF method to the simple, molecule-like systems in order to better understand the time evolution in this approach and to test the numerical precision of our method. As an example regimes of low and high frequency excitations are considered and compared with the adiabatic solution. On the second step we study properties of the collective excitations by analyzing the power spectrum of the metallic clusters subject to an ultrafast laser pulse. Our aim is to obtain information about the plasmon decay and compare it with available experimental data. This task looks very controversial in the framework of the TDHF approach. One may argue that the direct and exchange interaction taken into account in the method are not sufficient to describe a finite life-time, and one needs to consider correlations on the higher level of the theory. We give a thorough explanation of this paradox using a model system.
as an example.

As is shown in the theory section our method is fully \textit{ab initio}. Input parameters for the calculations are only the geometry of the cluster, number of electrons and parameters of the laser pulse. Geometry optimization of all clusters explored in the present work was done on the HF level by means of the \textsc{Gaussian} 98 quantum chemistry package. The initial guess of the geometry was taken from the publications and will be cited below. All systems we consider are closed-shell, i.e. the number of electrons with spin up and spin down is equal. Therefore we performed restricted HF calculations for the systems in the singlet state. Triplet states require spin-polarized calculations and will not be considered here.

\section{4.1 Deviation from adiabaticity}

We start our investigation with Na$_4$ (Fig. 4.1) – one of the most widely studied cluster in the literature. A small number of atoms made it accessible to almost all known \textit{ab initio} methods including CI \cite{51}, GW \cite{5} and TDLDA \cite{52}.

The cluster geometry is a planar rhombus with $D_{2h}$ symmetry. The result of the geometry optimization for this cluster is also widely reported in the literature, predicting this isomer as the most stable one. However, the bond lengths differ slightly depending on the level of theory and the basis set. The length of the rhombus side ranges from 3.27 Å in the LDA calculation \cite{53} to 3.74 Å in the HF approach \cite{54}. The length of the shorter diagonal is 2.87 Å and 3.25 Å respectively. Geometry optimization on a higher level of the theory gives similar results that fall inside these extremes.

We study the behavior of the Na$_4$ cluster within the TDHF and adiabatic approaches [compare Fig. 2.6(a)(c)]. At time $t = t_0$ the system is excited by a laser pulse with a temporal intensity distribution \cite{55}

\begin{equation}
I(t) = I_0 \cdot \text{sech}^2\left(\frac{t - t_0}{\sigma}\right) \quad (4.1)
\end{equation}

of a fixed duration and different photon frequencies. The results of the spectral analysis of the dipole response (power spectrum) and the excitation pulse are given in Fig. 4.2. The Fourier transform of the laser pulse peaks around the photon frequency and its width is inversely

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig41.png}
\caption{Top – geometry of the Na$_4$ cluster. Bottom – electronic density of the two highest occupied (1-2) and six lowest unoccupied (3-8) orbitals according to Ref. [5]. The two surfaces correspond to the constant density of, approximately, 0.001 a.u.$^{-3}$ and 0.002 a.u.$^{-3}$ Arrows denote allowed dipole transitions.}
\end{figure}
proportional to the duration of the pulse (see Fig. 4.4, dashed line). Thus, when the temporal width of the pulse is large compared to the period of one oscillation, the main contributions to the electron dynamics take place at the photon frequency. We follow the time evolution of the total energy of the system (Eq. (3.15)) and the number of the electrons (Eq. (3.13)) in the initially highest occupied (HOMO - 1\(b_{3u}\), see Fig. 4.1) and lowest unoccupied (LUMO - 1\(b_{2u}\)) molecular orbital states. The initial stationary HF calculation was done by employing the Los Alamos effective core potential (ECP) that replaces 8 inner electrons and use double zeta basis functions that contain two \(s\) and two \(p\) orbitals for each of the atoms. Thus we are left with 4 active electrons, that are described by 32 basis functions. In Fig. 4.1 two occupied and six lowest unoccupied eigenstates states are shown. Arrows denote allowed dipole transitions among the states. The adiabatic electron dynamics is obtained by performing the self-consistent solution of the HF equation with the perturbation operator for each of the time points.

The HOMO-LUMO gap in our approach is quite large (3.7 eV) and reflects the general feature of the Hartree-Fock method to overestimate the band gap. This is, however, consistent with a previous HF result (3.4 eV) reported in Ref. [51]. The LDA clearly fails in this case giving a band gap of only 0.55 eV. However GW calculation performed on top of LDA yields a systematically improved value of 3.0 eV [5]. The HOMO-LUMO gap gives only a crude approximation to the energy of the first excited state. Thus, information from the time-dependent calculation is required. The power spectrum that has been computed from the time-dependent calculations (Fig. 4.2, top) shows results similar to the experimental optical absorption spectrum (Fig. 4.2, bottom). In particular our calculation shows two strongly pronounced peaks at 2.3 and 3.1 eV observed as well in experiment at slightly lower energy. As is shown in a supercell GW calculation for this cluster they result from the transitions (see Fig. 4.1)
1b_{3u} - 2a_g (2-4); 1a_g - 1b_{2u} (1-3) and 1b_{3u} - 1b_{1g} (2-6); 1a_g - 1b_{1u} (1-5), respectively. In general, our calculations agree well with CI [51], GW [5] and TDLDA [52] calculations of excited states in the Na_4 cluster. A small shift to higher energies does not necessary mean a systematic tendency of TDHF to overestimate excited state energies. As we have shown above even stationary HF calculations can differ in predicting the HOMO-LUMO gap by up to 0.3 eV depending on numerical details, such as basis set size, use of the ECP, etc.

The difference between the power spectra obtained from high and low frequency excitations is only quantitative: the magnitude of the peaks increases approximately by one order of magnitude when the laser frequency approaches the resonance, preserving, however, their position. But, a completely different behavior has been found comparing the time evolution of the populations of the eigenstates and the total energy of the system. For excitations of an energy considerably lower than the energy of transitions between different states the dynamics of the system (Fig. 4.3) obtained from the full time-dependent treatment differs only slightly from that in the adiabatic approach.

After the excitation it returns almost to the initial state, preserving only some small oscillations. By contrast, a completely different behavior is found at higher frequencies (Fig. 4.4). Our calculations indicate that, in the case of a Na_4 cluster, for an excitation energy above 0.5 eV [Fig. 4.2(b)] the adiabatic approximation ceases to be valid and one has to resort to methods that explicitly account for the time dependence [compare Fig. 3.13(a) — adiabatic approximation and Fig. 3.13(c) — TDHF]. After the HOMO level is partially depopulated, it remains in that state forever, which, of course, is an effect, that cannot be observed on the adiabatic level. The time-dependence of the total energy reveals another feature of the method – energy conservation. After the perturbation is switched off the energy remains constant. This also provides a good test for the numerical precision of the ordinary differential equations (ODE) solvers that we used to propagate wave-functions in time. We have tested both Runge-Kutta and Bulirsch-Stoer methods with adaptive step-size. They give a perfect agreement and conserve total energy.
and particle number on the scale of hundreds of femtosecond with an accuracy of $10^{-6}$. Another possibility to study the high-frequency case would be to use Floquet theory [57], where the time-dependent Hartree-Fock or DFT equation is recast into a generalized eigenvalue problem. But as we found numerically it is very difficult to solve this kind of equation self-consistently.

### 4.2 SHG response

In Sec. 3.4 we have derived the second order nonlinear susceptibility $\chi^{\omega}_{ijk}$ using perturbation theory for the density matrix. In contrast to the linear response it is very sensitive to the geometry of the system, quality of the wave-functions and eigenenergies involved in the calculation. In particular, from the symmetry analysis one expects no second harmonic generation on systems with inversion symmetry. From an experimental point of view SHG is a valid method for the characterization of nanostructures and clusters. Recent investigations have examined, for example, the transient properties of SHG in silver island films [58], in specially designed silver particles [59] and Na clusters [60]. Employing observation of the size-dependence of the nonlinear response of Ref. [61] one can use the SHG measurements to characterize the distribution of the cluster size. Recently, the femtosecond time-resolved SHG from alkali metal clusters [62, 63, 64] was used to find life-times of the plasmon excitations. Compared to other techniques, such as linear optical measurements, the SHG scheme has the distinct advantage of eliminating the role of the substrate since the bare surface does not give an appreciable second harmonic response.

Here we would like to check the absence of SHG in the case of system with inversion symmetry and its appearance when the symmetry is broken by employing the eigenstates of the HF Hamiltonian used for the time-dependent calculation on the example of a Na$_4$ cluster. In order to break the inversion symmetry of the equilibrium geometry ($D_{2h}$) we allow for the displacement of one of the atoms of the cluster (Fig. 4.5). Apparently, this
4.2. SHG response

kind of distortion has no physical substantiation, serving only for the purpose to show the possibility to accurately compute the SHG response from clusters with broken inversion symmetry. However, one can expect a non-zero SHG signal even from the cluster with inversion symmetry at finite temperature due to the phonon distortion of the geometry\(^1\). Another possibility of getting non-zero response is to assume a situation close to experiment, where clusters are deposited on a substrate. This situation was theoretically studied in Ref. [34] by means of TDLDA.

In our case the HF equation is solved for each value of \(\Delta y\) in order to obtain the eigenenergies and wave-functions, which are subsequently used to compute the SHG response according to Eq. (3.38). We find that at zero displacement of the Na atom from the minimal energy position all matrix elements of \(\chi_{ijk}^{2\nu}(\omega)\) are zero within machine precision. At nonzero displacement we distinguish three groups of tensor elements:

- non-zero — \(|\chi_{ijk}^{2\nu}(\omega)| > 1.0 \cdot 10^{-6}\) (shown with bold face)
- almost zero — \(1.0 \cdot 10^{-6} > |\chi_{ijk}^{2\nu}(\omega)| > 1.0 \cdot 10^{-8}\) (shown with normal face)
- vanishing — \(1.0 \cdot 10^{-8} > |\chi_{ijk}^{2\nu}(\omega)|\) (are not shown).

\[
\chi_{ijk}^{2\nu}(\omega) = \begin{pmatrix}
(xxy) & (xyz) \\
(zxx) & (zyy) \\

(yyy) & (yzz)
\end{pmatrix}
\]

Our calculations show the reliability of the results of the HF calculation numerically fulfilling the selection rules with a high precision (the magnitude of non-zero tensor elements contradicting the selection rules is on the noise level, the smoothness of the graphs indicates a high precision of computing the dipole moments). A strong SHG response is observed in the region of energies from 2 eV to 6 eV in accordance with [34], where optimal frequency of the incident light is stated to be at 1/2 and 1 times the plasmon frequency.

As a possible development of the present technique two approaches are possible: using many-body wave-functions and excited states from the CI calculation to compute the SHG response according to the perturbation formula and performing a TDHF calculation. The present method, although being very simple, correctly accounts for the selection rules and, thus, can be used to describe future experiments. At the present time experiments are only possible on larger Na clusters of a size of tens of nanometers [62, 64].

\(^1\)SHG is also possible for systems with inversion symmetry when quadrupole transitions are taken into account.

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Fig. 4.5: Displacement of one the atom in \(Na_4\) cluster that breaks inversion symmetry and, therefore, enables nonzero SHG response. See text.
4.3 Finite life-time from TDHF theory

From the beginning we would like to distinguish two different approximations that form the essence of the time-dependent Hartree-Fock (TDHF) method. In the first step the stationary HF equation is solved in order to get the unperturbed ground state of the system. It contains no Coulomb correlation by definition. The Hartree-Fock Hamiltonian is Hermitian. It means that the energy of the quasi-particle states (eigenvalues of the HF equation) are pure real numbers, i.e. there is no imaginary part that would be responsible for the decay. In the second step the time evolution of the system is monitored by solving the TDHF equation Eq. (2.24). This equation does not only describe ground-state properties, but also excited states: particle-hole (\(ph\)) excitation and collective excitation — the plasmon.

To better understand how one can extract a finite life-time for the particle-hole states from the time-dependent HF calculations we continue to investigate the random interaction model described by the Hamiltonian Eq. (2.17), that contains \(m = 5\) particles distributed over the \(n = 10\) states. The one-particle energies are uniformly distributed in the energy interval \([-10,..0]\) and the two-particle interaction is given by a random Gaussian-shaped distributed potential with standard deviation \(\sigma = 1\).

The model is not a completely abstract object having no relation to realistic systems. Just on the contrary, a simple glance on the distribution of the matrix elements of the Coulomb interaction in clusters (Fig. 4.7) shows that they exhibit a great amount of

Fig. 4.6: SHG response of the Na\(_4\) cluster resolved as a function of displacement of one of the atoms. Absolute values of \(\chi_{zzz}\), \(\chi_{zyy}\) and \(\chi_{zxx}\) are shown.

Fig. 4.7: Distribution of the matrix elements of the Coulomb interaction for the Na\(_9^+\) cluster.
the randomness in their electronic properties. This fact leads to the idea that one can understand some general features of their spectra (Ref. [65]), as well as in other complicated systems like heavy nuclei Ref. [66] or mesoscopic quantum dots Ref. [67] on the basis of random matrix theory (Ref. [68]). We performed a series of time-dependent calculations for this model at different interaction strengths. The system is excited by changing the sign of interaction ($\alpha \to -\alpha$) at time $t = 0$.

As one can see from Fig. 4.8 at low interaction strength the power spectrum (Fig. 4.8) consists of a set of single peaks that correspond to the transitions of the particles between one-particle states. These states are degenerate, and increasing the interaction strength $\alpha$ leads to their splitting. Thus, at high resolution one sees a large number of $\delta$ peaks around each one-particle state. With low resolution, they essentially merge into one peak of non-zero width. Selecting an appropriate theoretical model, for example a Lorentzian for the decaying particle, one can fit the shape of this peak to that predicted from the model and obtain a finite life-time of the state. Thus one always has a choice in interpreting the results of a calculation or experimental observation. The only criterion that justifies a certain choice for the interpretation is the requirement that the natural width of the single peak in the envelope must be less than the distance between peaks, forming the envelope.

The situation with the plasmon life-time requires a more careful consideration. It was found long time ago that the collective-resonance states are composed as a coherent superposition of many $1\ ph$ states, in other words as a constructive interference [18, 69]. On the other hand, as we mentioned above, the time-dependent Hartree approximation (TDHF without exchange) in the limit of linear response is equivalent to the random

![Power spectra for the model (Eq. 2.17) with different interaction strength $\alpha$.](image-url)
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<table>
<thead>
<tr>
<th>System</th>
<th>Fig.</th>
<th>$N_{bf}$</th>
<th>$N_e$</th>
<th>$I_0[10^{11}\text{W/m}^2]$</th>
<th>$N_{ECP}$</th>
<th>basis set ref.</th>
</tr>
</thead>
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<td>Na$^+$</td>
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<td>72</td>
<td>4</td>
<td>107.6</td>
<td>10</td>
<td>[71]</td>
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<td>Pt</td>
<td>4.10</td>
<td>72</td>
<td>24</td>
<td>2.1</td>
<td>30</td>
<td>[72]</td>
</tr>
<tr>
<td>Pt</td>
<td>4.11</td>
<td>72</td>
<td>24</td>
<td>1.4-2.8</td>
<td>30</td>
<td>[72]</td>
</tr>
<tr>
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<td>4.12</td>
<td>15-25</td>
<td>5-10</td>
<td>0.0</td>
<td>30</td>
<td>[72]</td>
</tr>
</tbody>
</table>

Tab. 4.1: Parameters of the time-dependent calculation. As all systems are closed-shell $N_e$ means the number of spin-compensated electron pairs. $N_{ECP}$ is the number of electrons replaced by the effective core potential.

Phase approximation (RPA) of many-body perturbation theory [9]. The RPA dielectric function for the 3D uniform electron gas first derived by Lindhard [10] and its zeros, which are situated in the complex plane describe the electronic excitations in the system. There are two kinds of excitations in this approximation: particle-hole contributions and the plasmon. The life-time of the particle-hole excitations is finite on the RPA level and it explains why we are able to see a broadening in the above model. The plasmon excitation has no decay below a certain critical wave-vector $q$. But both the TDHF method and the RPA may yield a finite life-time for the plasmon. The Lindhard dielectric function is obtained from the RPA expression assuming an equilibrium electron distribution. In the case of finite temperature or an electron distribution away from equilibrium (which was studied in our case) the dielectric function must be evaluated in the whole complex plane. The plasmon frequency and decay can then be found at the intersection of the $\Re(e) = 0$ and $\Im(m(e)) = 0$ curves [12, 13, 70]. In our manuscript we study a situation close to experiment (such as described in Ref. [55]). The laser pulse interacts with a cluster and part of the photon energy is absorbed. The electron distribution becomes different from a step function and can be approximately treated introducing some effective non-zero temperature. For this case we expect to obtain a finite plasmon life-time from the TDHF method by analogy with the RPA result.

We believe that the shown illustrative examples clearly indicate the existence of a finite life-time of both the plasmon and the single-particle excitations in the time-dependent Hartree-Fock description of electron dynamics.

4.4 Power spectra of Na$^+_9$ and Pt$_3$ metal clusters

In simple systems, such as Na$_4$, the electronic density of states is small. This leads to a power spectrum with well separated peaks that correspond to one particle-hole (1ph) excitations. Considering more complicated systems such as Na$^+_9$ and Pt$_3$ (see Tab. 4.1 for the information about the number of basis functions, electrons in the active space and laser pulse parameters and Fig. 4.9), with a larger number of electrons, a new feature in their power spectra can be observed. Because of the dense level scheme in these clusters many 1ph states merge and form a collective excitation — a plasmon — due to their constructive interference. In contrast to one-particle excitations, the oscillator strength of
the plasmon is very high and it manifests itself as a strong peak in the power spectrum of the dipole moment. In contrast to the response function, which only characterizes the internal properties of the system, such as the energies and the oscillator strengths of the excited states, the power spectrum depends as well on the parameters of the external excitation. To study intrinsic properties of the system one has to minimize the role of the second factor. This can be done by putting the system initially in some nonequilibrium state and then following its relaxation [18] or one uses very short pulses, that embrace a large frequency interval.

We performed a series of calculations on Na\(^+\)_9 cluster for pulses of the mean photon frequency \(\omega = 2.25\) eV and different durations [Fig. 4.10 (left panel)]. The polarization of the electric field is taken to be along the axis of axial symmetry of the cluster. When the frequency width of the pulse is small predominantly states that correspond to the absorption of one, two, and three photons (denoted by vertical lines) are well pronounced. The plasmon peak at 2.7 eV is almost invisible [see Fig. 4.10 (left panel: a)]. Shorter pulses lead to a broader region of energies in which absorption can take place and thus excitations of the states that are further away from the resonance, but of higher oscillator strength become possible. Our value for the position of the plasmon peak, determined as a excitation with the highest oscillator strength that can be excited off-resonantly [Fig. 4.10 (left panel: c)] \((\omega_p = 2.7\) eV) of the Na\(^+\)_9 cluster is in good agreement with results obtained within the real-space implementation of TDLDA (Refs. [18, 73, 74, 75, 29]). In spite of this its oscillator strength is considerably lower in our approach. We think that this may be caused by the difference in the excitation mechanisms used (initial dipole shift of the entire electron cloud vs. excitation with certain frequency and time profile) and the number of electrons, taken into account. The plasmon, as a collective effect, is very sensitive to the density of virtual states in the system. Replacing part of the inner electrons with an effective potential may have small impact on the ground state properties, but may imply a sophisticated analysis in the case of excited states.

To better understand the possibility of the non-resonant plasmon excitation and in order to estimate the plasmon lifetime we apply our technique to the previously experimentally
studied cluster Pt$_3$ (Eberhardt and coworkers, Ref. [55]). It has been shown that the cluster possesses a very dense metallic like energy-level structure [76], leading to the enhancement of electron-electron scattering processes. The latter causes an effective energy transfer from one 1ph state to another, thus considerably reducing the plasmon lifetime in open-shell transition-metal clusters compared to noble or alkali-metal clusters. In calculations we use pulses of the same duration $\sigma = 0.76$ fs and different photon energies in a range from $\omega^* = 2.625$ eV to $\omega^* = 3.625$ eV that is in either case below the plasmon energy (Fig. 4.11). Polarization of the electric field is perpendicular to the plane of Pt$_3$ cluster. A typical time evolution of the density of occupied states, computed according to Eq. (3.14) is shown in Fig. 4.10 (right panel) ($n_i(t)$ is computed according to Eq. (3.13)). A transition of part of the electronic population from the occupied states close to Fermi level to previously unoccupied states occurs shortly after applying the laser pulse and leads to complicated oscillations. The use of very short pulses, although at present experimentally not feasible allows us to cover a very large energy range and to study fast processes far from resonance.

One can see (Fig. 4.11) a redistribution of the spectral weight of the peaks with the
4.4. Power spectra of Na$_9^+$ and Pt$_3$ metal clusters

Fig. 4.11: Power spectra of the Pt$_3$ cluster, excited with laser pulses of the same width and different photon energies: dotted line – $\omega^* = 2.625$ eV; dashed line – $\omega^* = 3.125$ eV; solid line – $\omega^* = 3.625$ eV. Right panel: comparison of the power spectra computed on different time intervals. Solid lines denote power spectra, calculated on the time interval after excitation took place, and dashed lines – power spectra on the whole time interval.

change of the excitation energy. The magnitude of the plasmon peak strongly depends on the vicinity of the photon frequency to the plasmon pole. The spectral weight of the shoulder in the region of energies 2-3.5 eV decreases when $\omega^*$ approaches the plasmon resonance at $\omega^\text{pl}=3.7$ eV. On the right panel of Fig. 4.11 for comparison power spectra computed in two different time domains are plotted. Dashed lines corresponds to that on the left panel, where power spectra are computed on the whole time interval: during the excitation and after it. Solid lines show power spectra computed on the second, relaxation period. One can see, that in this case the spectral weight is even more concentrated in the in plasmon peak, shoulders become less pronounced.

As mentioned above, the plasmon is a collective effect that originates from the strong enhancement of the one-particle excitations due to their constructive interference [18, 69]. If a time-dependent calculation is performed on very long time scales, it would be possible to resolve the plasmon peak as a very dense structure of individual 1ph peaks of very small width. In the higher-order correlation treatment these peaks will be smeared out to form one envelope that will resemble the plasmon peak at the present level of the theory (for the discussion of the plasmon width as a result of fragmentation of the resonance into nearby 1ph states and comparison with another mechanism — broadening due to the thermal fluctuations see Ref. [77]). That is why it is natural to use information from mean-field calculations in order to extract information about plasmon lifetime. The plasmon peak can be viewed as a Lorentzian or Gaussian peak. The first case describes a $e^{-t/\tau}$ decay of the quasiparticle in the many-body system, while the second one corresponds to the inhomogeneous broadening of the peak. The decay law is then $e^{-t^2/\tau^2}$. The lifetime can
differ up to a factor of $2\pi$ depending on the choice of the model\(^2\). We perform a non-linear fitting of the power spectrum by a set of Lorentzians (a similar idea can be found in the recent work of Molina et al. Ref. [78]):

$$P(\omega) = \sum_i \frac{A_i}{2\pi} \frac{\delta_i}{(\omega - \omega_i)^2 + \delta_i^2}$$

(4.2)

and find the width of the plasmon peak to be $\delta_{pl} = 0.17$ eV that corresponds to a lifetime of approximately $\tau_{pl} = 24$ fs ($\tau_{pl} = 3.8$ fs in the case of a Gaussian model). This result should be compared with experimental data of Eberhardt and coworkers, [55] who determined the lifetime to be less than 70 fs and attributed it solely to electron-electron scattering.

Up to now we were interested only in the properties of the system, excited in a way similar to the experiment. For comparison the clean (contains only the information about the properties of the system, but not of the laser pulse) power spectrum has been computed. To move the system out of equilibrium we used, as an initial configuration, the eigenstates of the HF Hamiltonian at elevated temperature ($T = 0.005$ a.u.). We propagate this solution during a very long time interval (several ps) to get a fine resolution for the spectra. A different number of basis functions and electrons has been included in the active space in order to understand its role on the formation of the plasmon peak (Fig. 4.12). Comparing this with the calculations using a larger basis set (Fig. 4.11), shows that only a small number of basis functions ($N_{bf} \sim 15 - 25$) is needed to get the correct position of the plasmon. However the fine details of the spectrum are quite sensitive to the size of the active space. Another important feature of the clean spectra is the presence of the peaks at 1-2 eV, not available for the case, when the system is excited by a laser pulse, which shows that some transitions might be forbidden for the particular polarization of the light, and can be excited only thermally.

Summarizing, in this chapter we demonstrated the application of a new computational scheme for the investigation of the electron dynamics in clusters under the influence of the external field within the mean-field approach. The application of the TDHF method to the Na\(^9\) cluster, previously intensively studied theoretically with different methods,\(^2\) For the Lorentzian model one has $Et = 2\pi\hbar$. This gives the relation $E[eV] t[fs] = \frac{6.6260755 \times 10^{-34}}{1.602188 \times 10^{-19} \times 10^{-15}} = 4.135642$. In the case of a Gaussian model $Et = \hbar$. Thus $E[eV] t[fs] = \frac{6.6260755 \times 10^{-34}}{2.141593 \times 1.602188 \times 10^{-19} \times 10^{-15}} = 0.658208.$
and the Pt$_3$ cluster already accessible to experimental investigation revealed the following capabilities of our approach:

- The method is able to accurately predict the position of the plasmon peak for the Na$_{9}^{+}$ cluster, although its oscillator strength differs considerably from the TDLDA result.

- The calculation on the open-shell transition metal cluster Pt$_3$ allowed us not only to determine the position of the plasmon resonance, but also to estimate its life-time by fitting the power spectrum to a set of Lorentzians. Our value for the decay constant supports the experimental evidence in favor of a bulk-like lifetime of the electronic excitations in this cluster despite an electronic structure that strongly differs from bulk Pt.

- The calculation on the TBRIM supports the possibility to determine the life-time of collective excitations from the time-dependent mean-field theory.