Chapter 6

Electron and proton impact ionization of $C_{60}$ and metal clusters

In the first part of this chapter we describe model potentials for the systems under study and their energy structure. In Sec. 6.2 the fluctuations in the electronic charge density of the clusters in response to an approaching electron are investigated for the electron impact ionization of $C_{60}$ and $Li_n$ clusters. The suppression of the single ionization channel is revealed by RPAE calculations and analyzed in the Thomas-Fermi model of screening. The interplay between finite size and nonlocal screening effects is studied by tracing the changes in the ionization cross sections for Li clusters with an increasing cluster radius. In Sec. 6.7 the role of exchange correlation is revealed by comparing the cross sections for proton and electron impact collisions.
6.1 Confining potentials

Due to the large number of electrons in the fullerene molecule, \textit{ab initio} calculations even of the single-particle wave functions and of the energy levels are practically impossible. They are performed, as a rule, within the frame of some phenomenological approach in which a model potential of fullerene shell is used, see e.g. [3, 15, 57, 89]. Naturally, preference should be given to a model that has the minimal set of fitting parameters. We employ the model having three experimentally observed parameters, namely, radius and thickness of the fullerene shell and the affinity energy of the electron to the singly charged fullerene.

The potential of \( C_{60} \), formed by carbon ions and localized core electrons, is replaced by a shifted potential well: \( V(r) = V_0 \) within the interval \( R - \Delta R < r < R + \Delta R \), and \( V = 0 \) elsewhere. Here \( R \approx 6.65 \ a_0 \) is the radius of the fullerene [85], the thickness of the shell is \( 2\Delta R \approx 2a_0 \), \( a_0 \) being the Bohr radius. The depth of the well is chosen such that to reproduce the experimental value of first ionization potential of \( C_{60} \), which is \( 7.1 \) eV [52, 75, 80] and to encompass 240 valence electrons. Despite the simple potential structure this model is a good tool for analytical estimations providing clear insight into phenomenology of the object and the processes under consideration. Moreover, as it will be shown in Sec. 6.2, the simple many-body improvement of this model done by the Hartree-Fock description of the eigenstates of the target together with the Thomas-Fermi approach for the interaction with the probe particle yields encouraging results when compared with available experimental data for electron impact ionization of \( C_{60} \) clusters.

Due to the shift \( R \) of the potential well from the origin (the center of spherical symmetry) the energy structure of the levels has an interesting form. An example of
this energy structure for the shifted square well is shown in Fig. 6.1. It consists of several branches, each branch is characterized by the fixed number of nodes of the corresponding wave function. Namely, the wave functions of the zero-branch (black curve in Fig. 6.1) have no nodes, states on the next branch (blue curve) have one node, etc. The levels belonging to the different branches are well separated in energy, at least for the small orbital momenta. The energy of the level on the same branch grows with the orbital number. With increase of the shell radius $R$ (with the constant potential width $2\Delta R$) the energy structure changes: the larger is the shift the more flat are the branches. In the limit, when the shift goes to infinity all branches transform to lines parallel to $x$-axis because all levels with the same number of nodes

![Eigenstate energies](image)

Figure 6.1: Example of the energy structure of the shifted rectangular well as a function of orbital momentum. Each branch of eigenstates is characterized by the fixed number of nodes $n_r$ of the corresponding wave function (black curve: $n_r = 0$, blue curve: $n_r = 1$, etc.)
In the large $R$ limit the centrifugal term gives negligible contribution. This behavior is clear from the Shrödinger equation. At large distances and large $R$ the centrifugal term becomes negligible with respect to $V_0$ (see Fig. 6.2) and the equation transforms to the one-dimensional equation for the finite square well:

$$-\frac{d^2 \psi_\ell(r)}{dr^2} + \left(\frac{\ell(\ell+1)}{r^2} - V_0(r \in [R \pm \Delta R])\right) \psi_\ell(r) = E \psi_\ell(r) \quad \rightarrow_{R \rightarrow \infty}$$

$$\rightarrow -\frac{d^2 \psi_\ell(r)}{dr^2} - V_0(r \in [R \pm \Delta R]) \psi_\ell(r) = E \psi_\ell(r). \quad \quad (6.1.1)$$

The quantum states of the clusters are constructed within the HF approximation. Hartree-Fock model is principally the best out of single-particle theories in a sense that it is able to incorporate part of electron-electron interactions and exchange. In this model each electron moves in a self-consistent averaged electric field of all the other electrons of the system, obeying Pauli principle. The one-electron potential then represents a sum of the ionic background and self-consistent electronic density.
of the valence electrons. The bound state wave functions are calculated in the frame of the nonlocal variable phase approach (Sec. 3.4). The eigenenergies are determined by finding the poles of the partial scattering amplitude on the imaginary semi-axis of the wavevector \( k = i\kappa, \kappa \in \mathbb{R} \). (c.f. Eq. 3.4.14).

In total, there are 16 occupied orbitals in \( C_{60} \). The lowest 10 of them are such that their wave functions with the orbital momenta \( 0 \leq \ell \leq 9 \) have no nodes. Then 4 orbitals with \( 0 \leq \ell \leq 3 \) have one node and two highest occupied orbitals with \( 0 \leq \ell \leq 1 \) have two nodes. Each orbital is \( 2 \cdot (2\ell + 1) \) degenerate. All shells are closed and the total number of the electrons is equal to 240. Lithium clusters with different number of atoms were chosen as an example of typical metallic particles. Basing on the same jellium potential model and within the VPA we performed the Hartree-Fock calculations of the eigenstates of \( Li_4, Li_8, Li_{18}, \) and \( Li_{44} \). The parameters of the rectangular well were again taken such that to reproduce the first ionization potential [29] and to contain all delocalized electrons.

Figure 6.3: The local part of one-electron HF potential of a) \( Li_{44} \) and b) \( C_{60} \), calculated in the spherical jellium and jellium shell models.
The self-consistent electronic density smoothes the sharp potential edges and introduces slight oscillations in the potential profile. The local parts of the self-consistent nonlocal one-electron potentials for the ground states of $C_{60}$ and $Li_{44}$ clusters are shown in Fig. 6.3

6.2 Manifestation of charge density fluctuations in metal clusters: suppression of the ionization channel

In this section we consider the influence of nonlocal screening on the single ionization of fullerene clusters by electron impact and show that the fluctuations of the electronic charge density of metallic clusters in response to an approaching electron suppress the single ionization channel. The present numerical results performed in the random phase approximation and analyzed by means of the Thomas-Fermi model of screening explain the behavior of the measured total ionization cross section for $C_{60}$. In addition, we investigate the interplay between quantum size and non local screening effects by tracing the changes in the ionization cross sections for $Li$ clusters with an increasing cluster radius.

The ideas sketched in the previous chapter are the key to resolve a yet open question of how metal clusters ionize in response to an external perturbation induced by an approaching electron. In the experiments, which have been performed using free $C_{60}$ clusters, one measures the absolute total ionization cross sections $W(\epsilon_0)$, i.e. the yield for the $C_{60}^{+}$ production, as function of the energy ($\epsilon_0$) of an incoming
electron [58, 34, 81]. These measurements confirmed repeatedly that the cross section \( W(\epsilon_0) \) possesses a plateau shape: Near the ionization threshold it rises strongly with increasing \( \epsilon_0 \) and then falls off slowly at higher energies. This saturation effect is markedly different from what is known for atomic targets where \( W(\epsilon_0) \) shows a pronounced peak at low \( \epsilon_0 \) (c.f. Fig. 6.4a).

Theoretical attempts to explain the behavior of \( W(\epsilon_0) \) for \( C_{60} \) are scarce. For the energy region \( \epsilon_0 < 100 \, eV \) only semi empirical models exist [27, 81] whereas for \( \epsilon_0 > 100 \, eV \) a quantum scattering approach has been proposed in Refs. [46, 45]. All of these previous theories [81, 27, 46, 45] were unable to explain the energy dependence of \( W(\epsilon_0) \), basically because the problem has been approached from an atomic scattering point of view without account for the influence of the fluctuating electron density on the scattering process which is of a key importance at low energies (\( \epsilon_0 < 1000 \, eV \)), as shown here in details: The central quantity that determines \( W(\epsilon_0) \) is the transition matrix element \( T(k_0, \phi_\nu; k_1, k_2) \). This matrix element is a measure for the probability that an incoming electron with momentum \( k_0 \) ionizes a valence electron bound to the state \( \phi_\nu \) of the cluster with a binding energy \( \epsilon_\nu \), where \( \nu \) stands for a collective set of quantum numbers that quantify uniquely the electronic structure of the cluster. The emitted and the scattered electrons’ states are labelled by the momenta \( k_1 \) and \( k_2 \). As outlined above the renormalized electron-electron interaction \( U_{\text{eff}} \) is determined by an integral equation with a kernel describing the particle-hole (de)excitation. Therefore, the evaluation of the \( T \) matrix entails a self-consistent solution of an integral equation. In the random-phase approximation with exchange [32] and within the post formulation [84] the \( T \) matrix has the form \( T_{RP\AE} = \langle k_1 k_2 \mid U_{\text{eff}} \mid \phi_\nu k_0 \rangle \) where (c.f. Eq. 5.2.9)
\[ \langle k_1 k_2 | U_{\text{eff}} | \phi_\nu k_0 \rangle = \langle k_1 k_2 | U | \phi_\nu k_0 \rangle + \] 
\[ + \sum_{\epsilon_p \leq \mu < \epsilon_h} \left( \frac{\langle \varphi_p k_2 | U_{\text{eff}} | \phi_\nu \varphi_h \rangle \langle \varphi_h k_1 | U | k_0 \varphi_p \rangle}{\epsilon_0 - (\epsilon_p - \epsilon_h - i\delta)} \right) - \left( \frac{\langle \varphi_h k_2 | U_{\text{eff}} | \phi_\nu \varphi_p \rangle \langle \varphi_p k_1 | U | k_0 \varphi_h \rangle}{\epsilon_0 - (\epsilon_p - \epsilon_h - i\delta)} \right) \] 
(6.2.1)

The spin averaged cross section \( W(\epsilon_0) \) is obtained from the weighted average of the singlet \( \propto |T^{(S=0)}|^2 \) (vanishing total spin \( (S = 0) \) of the electron pair) and the triplet \( \propto |T^{(S=1)}|^2 \) cross sections (we assume spin-flip processes to be irrelevant)

\[ W(\epsilon_0) = \frac{(2\pi)^4}{k_0} \int d^3k_1 d^3k_2 \left\{ \sum_{\nu} \frac{1}{4} |T^{(S=0)}(k_0, \phi_\nu; k_1, k_2)|^2 + \right. \] 
\[ \left. + \frac{3}{4} |T^{(S=1)}(k_0, \phi_\nu; k_1, k_2)|^2 \right\} \delta \left( \epsilon_0 + \epsilon_\nu - (k_1^2/2 + k_2^2/2) \right) \] 
(6.2.2)

In Eq. (6.2.1) \( \varphi_p \) and \( \varphi_h \) are respectively the intermediate particle’s and hole’s states with the energies \( \epsilon_p, \epsilon_h \) whereas \( \delta \) is a small positive real number. The first line of Eq. (6.2.1) amounts to a neglect of the electron-hole (de)excitations, as done in Ref. [45]. If \( U_{TF} \) is employed as an effective potential only the first line of Eq. (6.2.1) has to be evaluated and we obtain the much simpler expression \( T_{TF} = \langle k_1 k_2 | U_{TF} | \phi_\nu k_0 \rangle \) from which the cross section \( W_{TF} \) follows according to Eq. (6.2.2).

In contrast, as evident from Eqs. (6.2.1, 6.2.2), the numerical evaluation of \( W(\epsilon_0) \) within RPAE is a challenging task. To tackle this problem we proceeded as follows:

The quantum states of the metal clusters are constructed within the Hartree-Fock approximation and within the spherical jellium model. Alternatively, one can employ a model cluster potential as derived from the density functional theory (DFT)
within the local density approximation [45]. As shown below the DFT potential leads basically to the same conclusions as the model potential outlined above.

As remarked in Refs. [45, 46], the relatively large size of the cluster leads to severe convergence problems in evaluating the transition matrix elements. To circumvent this situation we utilized the nonlocal variable phase approach [7, 21, 47] for the numerical calculation of the Hartree-Fock states. We find that this choice for the numerical realization renders a rapid and a reliable convergence of the self-consistent calculations. Upon the numerical summation over the states \( \phi_\nu \) in Eq. (6.2.2) we carry out the six-dimensional integral over the momenta \( k_1 \) and \( k_2 \) using a Monte-Carlo procedure. To get an insight into the effect of the screening we calculated \( W_{TF}(\epsilon_0) \) for different values of the screening length \( r_0 \). As seen in Fig. 6.4(a), when approaching the unscreened limit \( (r_0^{-1} = 0.01 \text{ a.u.}) \), the calculated \( W_{TF}(\epsilon_0) \) agree well both in shape and magnitude with the finding of Ref. [27] at lower energies. At higher energies, the present model and the DFT calculations [45, 46] yield basically the same results. To simulate experimentally this atomic case let us assume the \( C_{60} \) molecule to be simply an ensemble of 60 independent carbon atoms in which case the cross section for \( C_{60} \) is a factor 60 larger than \( W(\epsilon_0) \) for atomic carbon [17]. The experimental cross sections we obtain by this procedure (Fig. 6.4(a)) agree very well with the shape of the calculated \( W_{TF}(\epsilon_0) \) at low screening. On the other hand, all of the theoretical models shown in Fig. 6.4(a) are clearly at variance with the measured \( W(\epsilon_0) \) for \( C_{60} \) (note the measured and the calculated cross sections are on an absolute scale). Fig. 6.4(b) sheds light on the underlying reasons for the shortcomings of the theories shown in Fig. 6.4(a): with increasing screening the region where scattering may take place shrinks. This results in a suppression of the ionization cross section.
Figure 6.4: (a) The total ionization cross-section (Eq. 6.2.2) for the electron impact single ionization of $C_{60}$ as function of projectile energy. The absolute experimental data (full squares) for the production of stable $C_{60}^+$ ions [58, 34] are shown along with the experimental electron-impact total ionization cross sections for atomic carbon (open circles) [17] multiplied by a factor of 60 (c.f. text). The solid line with crosses is the results of the DFT calculations [46] whereas the dashed line is due to the model of Ref. [27]. The dotted line indicates the present calculations with very small screening ($r_0^{-1} = 0.01$ a.u.). (b) The RPAE results (solid line) are shown together with calculations employing the Thomas-Fermi model of screening with varying values of the screening length, as shown on the figure. Full squares as in (a) whereas the open squares are the absolute experimental total counting cross-section for the emission of one electron from the initially neutral cluster (c.f. text for details) [58, 34].
with increasing screening length, as evident from Fig. 6.4(b). This effect is not a simple scaling down of \(W(\epsilon_0)\), but the shape is also affected. The peak of \(W(\epsilon_0)\) is shifted to higher energies and \(W(\epsilon_0)\) is generally flattened. In fact for extremely high screening the cross section is very small and shows basically very weak dependence on \(\epsilon_0\). This can be understood from the behavior of the form factor of the potential \(U_{TF}\) which for large screening is independent of \(\epsilon_0\), i.e. \(U_{TF}(q) \propto r_0^2 = \text{constant}, \ \forall \epsilon_0\). This behavior and the rough positions of the peaks in \(W(\epsilon_0)\) can be explained analytically if we write \(T_{TF} = \int d^3p_1 d^3p_2 \langle k_1 k_2 | U_{TF} | p_1 p_2 \rangle B\), where \(B = \langle p_1 p_2 | \phi_\nu k_0 \rangle\), and assume \(B\) to vary slowly with \(p_1, p_2\) on the scale of the variation of the form factor of \(U_{TF}\) (see Fig. 6.5 for illustration). Another extreme limit that shows up in Fig. 6.4 (c.f. also Fig. 6.6) is that when \(\epsilon_0\) is very large the electronic density of the cluster cannot react within the very short passage time of the electron through the interaction region and hence only small deviations between all the models are observed in the high energy regime.

The full numerical RPAE calculations for the cross section \(W_{RPAE}(\epsilon_0)\) confirm the trends we pointed out by means of the locally screened potential \(U_{TF}\). In fact by comparing the \(W_{RPAE}(\epsilon_0)\) and \(W_{TF}(\epsilon_0)\) one may deduce a rough estimate of the screening length which is of importance for the consideration of the relaxation time due to electron-electron collisions [28]. We obtain a qualitative agreement between \(W_{RPAE}(\epsilon_0)\) and \(W_{TF}(\epsilon_0)\) when \(r_0^{-1} = 0.3 \, a.u.\) is used to evaluate \(W_{TF}(\epsilon_0)\), however it should be stressed that we were not able to reproduce correctly the RPAE calculations by simply adjusting \(r_0\), as can be concluded from Fig. 6.4(b).

For a comparison of \(W_{RPAE}(\epsilon_0)\) with the experiments we recall the remarks of Ref. [27] that, experimentally the electron-impact on \(C_{60}\) may lead not only to the
Figure 6.5: Schematic illustration of the variation of the electron-impact ionization cross section as a function of the impact energy $E_0$ and the screening length $\lambda$:

$$
\sigma \sim \int d^3k_1d^3k_2 |U_{eff}(q)|^2 \cdot |\Phi(p)|^2 \sim \int d^3k_1d^3k_2 \left| \frac{1}{q^2+1/\lambda^2} \right|^2 |\Phi(p)|^2, \quad p = k_0 - k_1, \quad q = k_0 - k_1 - k_2.
$$

formation of stable $C_{60}^+$ but also may produce unstable $C_{60}^+$ that within a certain lifetime, not resolved by the experiment, decay subsequently into various fragmentation channels. Therefore, we show in Fig. 6.4(b) the experimental total counting rates, i.e. the total electron-impact ionization cross sections for the emission of one electron from $C_{60}$ along with the experimental total cross section for the ionization of $C_{60}$ and for the formation of the stable $C_{60}^+$ ion. We regard the agreement between the parameter-free $W_{RPAE}(\epsilon_0)$ and the experimental results as satisfactory, in view of the fact that the RPAE is the first order approximation to the two-point particle-hole Green function. To study the interplay between quantum-size effects and the nonlocal screening as described by RPAE we calculated within the spherical jellium model the cross section $W_{RPAE}(\epsilon_0)$ for Li clusters with varying sizes. For a judicious conclusions
Figure 6.6: The total electron-impact cross section for the ionization of spherical $Li$ clusters with varying radius size $R_{Li}$. (a) shows the RPAE calculations. (b) shows the results when the particle-hole (de)excitation is neglected (the first line of Eq. (6.2.1)). The insets in (a) and (b) highlight the low-energy region.
we normalized the cross sections to the number of electrons in the respective cluster. Figs. 6.6(a,b) reveals a striking influence of charge density fluctuation on $W(\epsilon_0)$ in particular at low energies: The RPAE model predicts a suppression of $W_{RPAE}(\epsilon_0)$ with an increasing cluster size due the increasing phase space for the particle-hole creation (c.f. inset of Fig. 6.6(a)). In contrast the neglect of charge density fluctuations results in increased peak values of $W(\epsilon_0)$ for larger clusters. Furthermore, according to the RPAE, the peak in $W(\epsilon_0)$ is considerably broadened and shifted towards higher energies when the cluster size is increased (for the cluster with a radius $R_{Li} = 4a_0$ the peak is at $\epsilon_0 \approx 200\,eV$ whereas this peak is shifted to $\epsilon_0 \approx 700\,eV$ for $R_{Li} = 10a_0$) (c.f. Fig. 6.6(a) and inset). As explained above, this is consistent with the behavior of $W(\epsilon_0)$ with increased screening length. In contrast, the neglect of the particle-hole (de)excitations leads to cross sections with the peak positions being shifted towards lower energies as the cluster size grows (c.f. Fig. 6.6(b) and inset). For small clusters or for $\epsilon_0 \gg 1$ there is hardly an influence of charge density fluctuations (c.f. heavy solid lines in Fig. 6.6(a,b)).

Summarizing the above results, we have seen how the particle-hole (de)excitations suppress and modify the ionization cross sections for the electron scattering from neutral metal clusters. The simple Thomas-Fermi (TF) model of screening provided a useful tool to obtain global views on the role of delocalization of the electrons. The more elaborate random phase approximation confirmed and specified more precisely the understanding gained from the TF model. We also envisaged the inter-relation between quantum-size and screening effects. From a formal point of view, we note that to treat scattering processes in isolated few charged particle systems, such as in atoms
or small molecules, one has to deal with the infinite-range tail of the Coulomb interaction that precludes the use of standard methods [84] and induces multiple scattering between the collision partners up to very large distances. In contrast, the presence of the screening in systems with a large number of delocalized active electrons renders possible the use of standard scattering theory but on the considerable expense of actually calculating the nonlocal screening properties of the medium, e.g. as described by the polarization propagator $\Pi$. The crossover between the two cases is marked by a breakdown of the RPAE for dilute systems, where other methods such as the ladder approximation become more appropriate. In any case one has to bear in mind that, both from a practical and a conceptual point of view, approximate methods that perform well for few particle scattering may not be suitable for the treatment of delocalized many-particle systems (and vice versa).

6.3 Ionization by proton impact: estimation of exchange effects

With the use of particles and antiparticles as projectiles in collision experiments, many effects related to the projectile charge and mass have been identified, and a detailed picture of phenomena influencing single and multiple ionization of atoms have been obtained [50, 77]. Complete set of data for ionization of the system by $e^+$, $e^-$, $p^+$, $p^-$ allows to trace the role of polarization and exchange effects. At high impact velocities, much greater than the characteristic velocity of target electrons, all four particles have the same ionization cross section. Therefore in the high energy limit the cross sections should merge. At lower velocities the positive particles generally
have higher ionization cross sections, as expected from polarization effects. Electron-impact ionization differs from the other three collisions in the indistinguishability of the projectile and the target electrons. Exchange interaction is a part of Coulomb interaction, originating from specific correlation in the movement of electrons caused by the symmetry of the coordinate part of the electronic wave function. Mathematically, in the case of $e^-$ and $e^+$ scattering the only difference in the ionization matrix element is the exchange term, which is absent for the proton impact. As for electrons of the target, they, of course, have exchange interaction in both cases. In Fig. 6.7 the

![Figure 6.7: Electron and proton impact ionization of C$_{60}$: black curve – RPA calculations for proton impact; red curve – RPAE calculations for electron impact; filled symbols – experimental data for proton impact [86]; open symbols – experimental data for electron impact ionization of C$_{60}$ [34, 58]; blue curve – calculations of [67] with one adjustable parameter.

single-ionization cross sections for electron- and proton-impact ionization of C$_{60}$ are shown as a function of the projectile velocity (in atomic mass units). The polarization
of the fullerene molecule is accounted by RPAE. The electron-hole excitations are accounted by summation over all possible states of the discrete and continuum spectra of $C_{60}$ obeying the energy conservation. As discussed above, at high impact energy $\sim 1 \, keV$ the two curves begin to merge. At the intermediate energies due to different polarization of the fullerene by proton and electron, the difference between the cross sections is most prominent and maximal at $\sim 170 \, eV$, where the curves differ by $\sim 30\%$. Interesting to note very close low-energy behavior of the cross sections.