Atoms as many-body systems

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Abstract. Contrary to common wisdom, not everything is clear and simple in the structure of many-electron atoms. Complexity in atoms is mainly a result of interelectron interaction that leads to rather unusual behaviour. Most transparently this is manifested in photo-ionization processes of many-electron atoms and some multi-atomic objects e.g. endohedrals. Particular attention will be given to the approach describing the interaction of photons with many-electron atoms in the frame of the many-body theory based on the Feynman diagrams technique. As a suitable one-electron approximation the Hartree - Fock (HF) approach will be presented. On its ground we will include the so-called electron correlation effects and discuss the frequently used Random Phase Approximation with Exchange - RPAE. Some results of recent calculations will be presented.

1. Introductory remarks

Historically, atoms with nuclear charge more than one were the first objects for developing quantum – mechanical many-body theory. A number of ideas and methods from atomic theory were then successfully applied in other areas of physics, particularly in nuclear physics. Here as good examples serve the shell model, Hartree-Fock (HF) method, spin-orbit interaction. The latter became now a fertilizing idea in solid-state physics. In its turn, atomic physics theory acquired Random phase approximation from electron gas theory and nuclear physics. It appeared that analogs to nuclear Giant dipole resonances were found in a number of atoms. Very successful was the application of the general quantum many-body theory with inclusion of Feynman diagrams. This approach permitted to understand deeply the processes of photoionization and electron scattering, paving the way to prediction of a number of different resonances, such as interference, continuous spectrum autoionization and spin-doublet resonances [1].

Specific features of complex atoms, contrary to nuclei, are the high accuracy, with which the inter-electron interaction is known, and the fact that the electron distribution is strongly inhomogeneous. Therefore, one has to start with the numerical implementation of HF and build on it many-body approaches self-consistently in order to escape the danger of double counting of the same effects. Among such theories the random-phase approximation with exchange (RPAE) [2] is the most successful. The use of this approach not only permits to describe most essential atomic processes, such as photoionization, electron scattering and vacancy decay, but to understand deeply the methods applied, which is essential in operating with this method in other domains, e.g. nuclear physics.

As objects of concrete calculations, we consider closed and semi-closed shell atoms and spherical endohedrals, i.e. fullerenes C_{60} with noble gas atoms stuffed inside.
2. Specifics of HF

The HF or self-consistent field equation looks like a simple one particle Schrödinger-type equation, with at first glance non-essential differences. Namely, they are nonlinear and non-local, as is seen in (1), presented in atomic units, with electron mass $m$, charge $e$ and Planck constant $\hbar$ being equal to 1:

$$[-\Delta / 2 - Z / r + \int d\vec{r}' \rho(\vec{r}') / |\vec{r}' - \vec{r} - E_i|] \phi_i(\vec{r}) = \sum_{i \neq F} \int d\vec{r}' \phi'_i(\vec{r}') \phi_j(\vec{r}) / |\vec{r}' - \vec{r}|.$$  \hfill (1)

Here $Z$ is the nuclear charge and the summation on the r.h.s. is performed over all occupied states.

These modifications lead to profound alterations in qualitative features of the solutions of (1) \cite{3}. The exchange leads to alteration of the asymptotic behavior, from depending upon the respective binding energy of state $\phi_j(r)_{r \to \infty} \sim \left[ \exp(-2\sqrt{E_k}|r|) / r^{l+1} \right]$ to

$$\phi_j(r)_{r \to \infty} \sim \sum_o a_{jl,o} \left[ \exp(-2\sqrt{E_o}|r|) / r^{l+1},$$ \hfill (2)

where $o$ denotes outer relative to $k$ atomic states and $E_o$ is the outermost binding energy. This alteration modifies dramatically the ionization of inner electrons $|E_k| \gg |E_o|$ under the action of a strong field.

The exchange increases the number of zeroes $n_l$ in the radial wave function, leading to a violation of a well-known relation, which now reads $n_l \geq n - l - 1$, where $n$ is the principal quantum number and $l$ is the angular momentum of the electron state considered. Due to non-locality, the HF equations become Gauge non-invariant in the sense that instead of the familiar relation $\nabla = \mathbf{p}$ one has $\vec{\nabla} i \mathbf{H} \mathbf{r} \mathbf{p} \neq \mathbf{p}$. As a result, we have two instead of one definitions of the photon-electron interaction operator.

Due to exchange, the Levinson theorem for elastic scattering phase shift at zero energy $\delta_j(E = 0)$ is violated, becoming $\delta_j(E = 0) = (q_j + t_j)\pi \geq q_j\pi$, where $q_j$ is the number of projectile-atom bound states (see \cite{3} and references therein).

3. RPAE equations and photoionization resonances

The RPAE equation can be presented symbolically in a very simple operator form \cite{1}:

$$\hat{D}(\omega) = d + \hat{D}(\omega) \hat{\chi}(\omega) U \text{ or } \hat{D}(\omega) = d / \left[ 1 - \hat{\chi}(\omega) U \right],$$ \hfill (3)

where $\hat{D}$, $d$ are the photon absorption operators in RPAE and HF, respectively, $\hat{\chi}(\omega)$ is the electron-vacancy propagator and $U$ is the combination of direct and exchange Coulomb inter-electron interaction. Powerful broad structures that appear in the amplitude $\hat{D}(\omega)$ and in the photoionization cross-section are called Giant resonances. They are results of the fact that at some $\omega = \omega_{GR}$ the following relation holds: $\left[ 1 - \hat{\chi}(\omega_{GR}) U \right] = 0$.

Of interest are also cases when matrix elements of $\hat{D}(\omega)$ are close to zero, while those of $d$ are not. The corresponding structures are called interference resonances. Particularly strong is the mutual effect of subshells closely located in energy. Note that, depending upon absorbed photon frequency, the multi-electron subshells can act as resonators, mirrors and amplifiers. As a result, the photoionization cross-sections become quite complex functions of photon frequency (see \cite{1} and references therein).
The investigation of atomic photoionization helped to reveal a number of other resonances, like Giant autoionization, Continuous spectrum photoionization and Intra doublet resonances. As far as I know, their counterparts in nuclear physics are neither found nor even predicted.

4. Non-dipole contribution to photoionization

The multi-electron effects in atomic photoionization are strong in the frequency region, where the dipole approximation is valid. Quadrupole corrections are suppressed by the factor \( (\omega R / c)^3 << 1 \), where \( R \) is the atomic radius and \( c \) is the speed of light. Therefore, the quadrupole contribution itself to the photoionization cross-section is almost non-observable. However, the angular distribution of photoelectrons is formed by superposition of different photoelectron partial waves. As a result, the ratio of contributions of quadrupole-to-dipole terms in the angular distribution is much bigger, namely of the order of \( (\omega R / c)^3 << 1 \). The general expression for the angular photoelectron distribution due to the absorption of non-polarized light is given by the equation (see, e.g. [1])

\[
\frac{d\sigma_{nl}(\omega)}{d\Omega} = \frac{\sigma_{nl}(\omega)}{4\pi} \left\{ 1 - \frac{\beta_{nl}(\omega)}{2} P_2(\cos \theta) + \frac{\omega}{c} \left[ \gamma_{nl}(\omega) P_1(\cos \theta) + \eta_{nl}(\omega) P_3(\cos \theta) \right] \right\},
\]

where \( nl \) are the ionized subshell quantum numbers and \( P_{j=1,2,3}(\cos \theta) \) are the Legendre polynomials. The parameters in (4) are complicated functions of dipole and quadrupole matrix elements and photoelectron scattering phases. A specific feature of (4) is an asymmetry of the non-dipole terms relative to forward-backward direction of the photoelectrons \( (\theta \rightarrow \pi - \theta) \), which results in a preferential direction of the photoelectrons along or opposite to the photon flux momentum. It leads to macroscopic electric currents that were named "drag" currents, a not yet observed phenomenon [4].

As an example, we present the simplest expression for the angular anisotropy parameter – for s-subshells

\[
\gamma_{n0}(\omega) = -\eta_{n0}(\omega) = \frac{6Q}{5D} \cos(\delta_1 - \delta_2),
\]

where \( Q, D \) are the absolute values of quadrupole and dipole matrix elements and \( \delta_1, \delta_2 \) are dipole and quadrupole photoelectron phases that include scattering phases and phases of the corresponding matrix elements. Resonance enhancements of \( \gamma_{n0}(\omega) \) are due to maxima in \( Q \), minima in \( D \) and phase resonances in the last term in (5) that happen when \( \cos(\delta_1 - \delta_2) \rightarrow 1 \).

5. Photoionization of endohedrals

Recently, the photoionization process of endohedrals attracted considerable interest. Most attention is given to studies of a \( C_{60} \) fullerene molecule stuffed with a noble gas atom A, \( A@C_{60} \) (see e.g. [5]). Microscopically, such a system can be treated as a sort of an atom, entirely in the frame of HF and RPAE methods for all interacting electrons of this object moving in the fields of 60 carbon nuclei and A atom nucleus. However, such an approach is too complicated to be numerically implemented. Instead, one can take into account that the \( C_{60} \) shell is thin enough and its radius \( R_c \) is much bigger than the atomic radius \( R_A \). For low enough \( \omega \) its structure is inessential and \( C_{60} \) can be substituted by a spherically-symmetric homogeneous electric charge distribution, similar to another multi-electron shell quite far from atom A [5].

Having this in mind, one can separately take into account two effects that influence the photoionization of the stuffed atom. The first is the reflection of the photoelectron leaving the atom A by the static field of the \( C_{60} \) shell. This can be taken into account by adding the static field of \( C_{60} \) in the HF equation for the A atom. In some cases this effect can be taken into account simply by multiplying
the atomic A photoabsorption amplitude by a factor $F_l(p)$, where $l$ and $p$ are the angular momentum and the modulus of the linear momentum of the outgoing electron.

The other effect is the modification of the photon beam acting upon atom A due to polarization of the $C_{60}$ electron shell under the action of this photon beam. This effect is taken into account by introducing the polarization factor $S(\omega)$ that is expressed via the dipole polarizability of the $C_{60}$ electron shell.

There exist two-shell endohedrals, of which an example is A@C$_{60}$@C$_{240}$ that can be treated as an atom A surrounded by two reflecting and highly polarizable shells [6].

6. Resonances in endohedral atoms.

The presence of fullerene shells brings in a multitude of different resonances. Particularly rich is the structure of the photoionization cross-section for two-shell endohedrals. We limit ourselves to one-shell endohedrals, for which confinement (exemplified by Figure 1) and Giant endohedral (exemplified by Figure 2) resonances are most impressive. While the former result are results of interference phenomena due to photoelectron waves scattering by the fullerenes shell, the latter reflect the combined effect of photoelectron scattering by the fullerene shell and dependence of the fullerene dipole polarizability upon $\omega$ that is taken into account by the factor $S(\omega)$. Giant endohedral resonances have cross-sections that are bigger by a factor up to 10-20 than for the isolated atom A. As is seen, the corresponding cross-section reaches 1000 Mb, while for an isolated atom it is only 80 Mb.

![Figure 1. Confinement resonance of 4d-electrons for Xe@C$_{60}$, in RPAE.](image1)

![Figure 2. 5p-electrons Giant endohedral resonance for Xe@C$_{60}$, in RPAE](image2)

7. Concluding remarks

We demonstrated impressive examples of many-body effects in photoionization of atoms and endohedrals. They manifest themselves in a number of new resonances that await experimental detection. However, it is essential to note that similar effects are very important in electron scattering upon atoms and endohedrals and decay of vacancies created in the scattering processes. A number of new reaction channels open when the inter-electron interaction is taken into account. As in the considered processes of photoionization, many-electron corrections to processes, which are possible in one-electron approximation, are of great importance, too.

References
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