



Some remarks on configuration-interaction and J-matrix approach to multi-ionization of lithium atom

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Introduction

One of the fundamental processes in atoms exposed to laser light is multiple ionization. Two primary types of multiple ionization has to be recognized, namely the sequential one and the non-sequential one. The first one may be treated by an independent electron model (e.g. Starace 2005). The non-sequential case, where the electron correlation is very important, may be treated by time dependent method based on a spectral method of configuration-interaction type. Here, J-matrix method calculations play important role in extracting some of the ionization channels (Foumouo et al 2006, Foumouo et al 2008).

In this contribution, we discuss the theoretical approach to the one-, two- and three-photon single, double and triple ionization of lithium atom, interacting with an ultrashort XUV pulse. We assume that the atom possess an infinitely heavy nucleus and use atomic units in all formulas.

Atomic structure

Energy levels E_n and corresponding wave functions Ψ_n^{LM} can be found by solving the stationary Schrödinger equation

$$H\Psi_n^{LM}(\vec{x}) = E_n\Psi_n^{LM}(\vec{x}), \quad (1)$$

where $\vec{x} \equiv r_1, r_2, r_3$ is the set of electronic coordinations. H is the non-relativistic Hamiltonian:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{31}} \quad (2)$$

The equation (1) for total angular momentum L and its projection M can be solved by means of MOLPRO package (e.g. calculations for Li_2 , Jasik and Sienkiewicz 2006). In principle, this program can also provide same wave functions for the continuum spectra, but it would require some massive change in the code. Other way, proved already to be successful (Foumouo et al 2006), uses spectral expansion of the atomic states.

In the case of so-called explicitly correlated base, one may try to use the functions based on Hylleraas helium function, adapted to the lithium in the form

$$\varphi(\vec{x}) = r_1^{a_1} r_2^{b_1} r_3^{c_1} r_{12}^{d_1} r_{23}^{e_1} r_{31}^{f_1} e^{-\alpha_1 r_1} e^{-\alpha_2 r_2} e^{-\alpha_3 r_3} \quad (3)$$

In order to factorize the electron-electron terms in (2), the multipole expansion can be used:

$$\frac{1}{r_{ij}} = \sum_{q=0}^{\infty} \sum_{m=-q}^q \frac{4\pi}{2q+1} \frac{r_i^q}{r_j^{q+1}} Y_{qm}^*(\theta_i, \varphi_i) Y_{qm}(\theta_j, \varphi_j), \quad (4)$$

where $r_c = \min(r_i, r_j)$, and $r_s = \max(r_i, r_j)$.

In principle, the eigenfunction of eq. (1) can be expanded in products of three one-electron Coulomb-Sturmian functions S_{nl}^m with the angular part completed by three spherical harmonics:

$$\Psi_{n_1 n_2 n_3}^{LM} = \sum_{l_1 l_2 l_3} \sum_{m_1 m_2 m_3} \sum_{m} \Psi_{l_1 l_2 l_3}^{LM} S_{n_1 l_1}^{m_1} S_{n_2 l_2}^{m_2} S_{n_3 l_3}^{m_3} A_{l_1 l_2 l_3}^{LM} Y_{LM}(\hat{r}) \quad (5)$$

Putting the above expansion into the residued equation (Finlayson 1972):

$$R_N(\vec{x}) = (H - E)\Psi_{n_1 n_2 n_3}^{LM}(\vec{x}), \quad (6)$$

one obtain the algebraic equation for coefficients $\Psi_{l_1 l_2 l_3}^{LM}$:

$$HW = ES\Psi. \quad (7)$$

Time propagation

The time-dependent Schrödinger equation (TDSE) for a lithium atom exposed to an oscillating field:

$$i\frac{\partial}{\partial t}\Psi(\vec{x}, t) = [H + D_G(t)]\Psi(\vec{x}, t), \quad (8)$$

where H is the atomic Hamiltonian given by (2). Here, $D_G(t)$ describes the dipole interaction of the system with the oscillating field in the length gauge ($G \equiv L$):

$$D_L(t) = \vec{E}(t)(\vec{r}_1 + \vec{r}_2 + \vec{r}_3), \quad (9)$$

or velocity gauge ($G \equiv V$):

$$D_V(t) = -i\vec{A}(t)(\vec{\nabla}_1 + \vec{\nabla}_2 + \vec{\nabla}_3). \quad (10)$$

$\vec{E}(t)$ is the electric field, and $\vec{A}(t) = zA_0 f(t) \sin \omega t$ is the corresponding vector potential. It oscillates at the frequency ω and is linearly polarized along the z axis. Finally $f(t)$ is the pulse envelope, equal to $\cos^2 \frac{t}{2}$ when $|t| \leq \frac{\tau}{2}$, and 0 otherwise.

Projection of TDSE onto basis (5) gives us system of first-order differential equations. They can be solved e.g. by using a Runge-Kutta type method.

Continuum wave functions

The total wave packet after the end of time propagation:

$$\Psi_{total} = c_0 \Psi_{BS} + c_1 \Psi_{SC} + c_2 \Psi_{DC} + c_3 \Psi_{TC}, \quad (11)$$

where Ψ_{BS} is the bound-state component, Ψ_C is the continuum-state component and is the linear superposition of single- (Ψ_{SC}), double- (Ψ_{DC}) and triple-continuum (Ψ_{TC}) multichannel scattering wave functions. To distinguish these particular continuum states, one should project the final (ionized) wave packet (after the interaction with laser field) on the corresponding multichannel wave function associated to the single, double or triple continuum.

By solving the equation (7), one gets bound atomic states and approximate continuum state (pseudostates).

- When the total energy E is below the single-ionization threshold, the eq. (7) describes the bound states.
- When the total energy E is above the single-ionization threshold but below the double ionization, one gets the pseudostates with the one electron in continuum.
- If E exceeds the double ionization threshold but still is below the triple one, then eq. (7) describes pseudostates with one bound electron and two continuum electrons.
- At last, when E is above triple-ionization energy, all electrons are in continuum.

The J-matrix method

In general, the J-matrix method is one of the algebraic methods in quantum scattering theory. It allows to find an approximate solution of the scattering problem on the radial potential $V=V(r)$. The method is based on fact, that the radial kinetic energy operator is tridiagonal in some suitable bases - forms so called Jacobi matrix.

Now, to describe the method (in its original version for potential scattering), let's start again with stationary Schrödinger equation:

$$\left(H_0 - \frac{\hbar^2 k^2}{2} + V\right)\Psi = 0, \quad (12)$$

where $H_0 - \frac{\hbar^2 k^2}{2} \equiv -\frac{1}{2}\nabla^2 + \frac{\hbar^2 l(l+1)}{2r^2} - \frac{\hbar^2 k^2}{2}$ is the radial kinetic energy operator, $k = \sqrt{2E}$ - wave number, $V = V(r)$ - scattering potential.

Now let's choose a basis set $\{\phi_n\}_{n=0}^{\infty}$, that

$$J_{mn} \equiv \left\langle \phi_m \left| \left(H_0 - \frac{\hbar^2 k^2}{2}\right) \phi_n \right. \right\rangle \neq 0 \text{ only for } m = n, n \pm 1. \quad (13)$$

Obtained so called Jacobi form (or the J-matrix)

$$J_{mn} = \begin{pmatrix} \times & \times & 0 & 0 & 0 & 0 & 0 \\ \times & \times & \times & 0 & 0 & 0 & 0 \\ 0 & \times & \times & \times & 0 & 0 & 0 \\ 0 & 0 & \times & \times & \times & 0 & 0 \\ 0 & 0 & 0 & \times & \times & \times & 0 \\ 0 & 0 & 0 & 0 & \times & \times & \times \\ 0 & 0 & 0 & 0 & 0 & \times & \times \end{pmatrix} \quad (14)$$

is tridiagonal, symmetric and real.

One of the basis sets fulfilling the condition (13) is the Coulomb-Sturmian basis set, which is complete and square-integrable:

$$S_{nl}^m(r) = N_{nl}^m r^{l+1} e^{-kr} L_n^{2l+1}(2kr), \quad (15)$$

where k is real, nonlinear parameter, $L_n^{2l+1}(2kr)$ is a Laguerre polynomial. The other choice of basis functions is a gaussian basis set. Functions (15) are solution of the Sturm-Liouville equation:

$$\left[\frac{1}{2} \frac{d^2}{dr^2} + l(l+1) - \frac{\chi}{r} + \frac{k^2}{2} \right] S_{nl}^m(r) = 0. \quad (16)$$

The normalization constant N_{nl}^m in eq. (15) can be derived from the condition $\int_0^\infty S_{nl}^m(r) S_{n'l'}^m(r) dr = 1$ and written as

$$N_{nl}^m = \sqrt{\frac{2}{n}} (2k)^{l+1} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \quad (17)$$

Let us stress, that elements of the J-matrix (13) can be easily calculated in the selected basis set.

To generate scattering wave function, we solve the regular and irregular equations:

$$\begin{aligned} \left(H_0 - \frac{\hbar^2 k^2}{2}\right) \hat{S}(k, r) &= 0 \\ \left(H_0 - \frac{\hbar^2 k^2}{2}\right) \hat{C}(k, r) &= -\frac{1}{2k} \phi_0^m(kr) \end{aligned} \quad (18)$$

to fulfill the required asymptotic behavior:

$$\begin{aligned} \hat{S}(k, r) &= \sum_{n=0}^{\infty} s_n^m \phi_n^m(kr) e^{i\pi n} \sin\left(kr - \frac{\pi}{2}\right) \\ \hat{C}(k, r) &= \sum_{n=0}^{\infty} c_n^m \phi_n^m(kr) e^{i\pi n} \cos\left(kr - \frac{\pi}{2}\right) \end{aligned} \quad (19)$$

Now, the following relations are satisfied: $\sum_{n=0}^{\infty} J_{nn} s_n^m = 0$, $\sum_{n=0}^{\infty} J_{nn} c_n^m = -\frac{1}{2k} \phi_0^m$, $J_{00} s_0^m + J_{01} s_1^m = 0$, $J_{00} c_0^m + J_{01} c_1^m = -\frac{1}{2k}$, $J_{n,n-1} c_{n-1}^m + J_{n,n} c_n^m + J_{n,n+1} c_{n+1}^m = 0$; $n = s, c, n > 1$, and the expansion coefficients s_n^m and c_n^m can be easily found (Heller and Yamani 1974, Yamani and Fishman 1975). Now, by replacing the original scattering problem by the new problem by truncating the scattering potential V in selected basis, one can find the solution of this new problem in an algebraic way, thus find the approximate solution of the original problem.

Role of the J-matrix method in multi-ionization

In the multi-ionization problem, the multichannel J-matrix method can be used in LS coupling scheme (Broad and Reinhardt 1976), to generate scattering wave function associated with the double- and triple-ionization channels of the lithium atom (Ψ_{DC} and Ψ_{TC} in eq. 11).

In particular, the J-matrix method may be used to solve the partial-wave close-coupling equations. It is connected with the fact, that Hamiltonian associated with pure hydrogenic system can be analytically diagonalized in a basis (15). This approach bear close resemblance to R-matrix theory, as the configuration space is divided into two regions: the inner one, in which the space is spanned by a Sturmian basis to solve the stationary Schrödinger equation, and the outer one, in which the outgoing electron is moving in the screened Coulomb potential (Broad and Reinhardt 1976, Foumouo et al 2008).

Truncation of the perturbing potential in finite basis set (15) provides a numerical method closely related to that of bound-state configuration interaction, and having the advantage that e.g. scattering information may be obtained over a continuous range of energies from a single major computational step.

Having the double- and triple-continuum components (Ψ_{DC} and Ψ_{TC}) calculated, one can obtain the single-continuum component (Ψ_{SC}), by subtracting the bound-state component (Ψ_{BS}) and double- and triple-ionization components (Ψ_{DC} and Ψ_{TC}) from the total wave packet Ψ_{total} . Then, the single-, double- and triple-ionization probabilities can be calculated.

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