Eur. Phys. J. Plus (2015) **130**: 170
DOI 10.1140/epjp/i2015-15170-9

The European Physical Journal Plus

Regular Article

Construction of the energy matrix for complex atoms Part IV: Excitation of one electron from a closed shell into an open shell

Magdalena Elantkowska[1,a], Jarosław Ruczkowski[2], and Jerzy Dembczyński[2]

[1] Laboratory of Quantum Engineering and Metrology, Faculty of Technical Physics, Poznań University of Technology, Piotrowo 3, 60-965 Poznań, Poland
[2] Institute of Control and Information Engineering, Faculty of Electrical Engineering, Poznań University of Technology, Piotrowo 3A, 60-965 Poznań, Poland

Received: 30 June 2015 / Revised: 28 July 2015
Published online: 25 August 2015

Abstract. This work is a continuation of the previous series related to the construction of the energy matrix for complex atoms. The effects of the second-order configuration interaction perturbations on the energy-level structure of nl^N, $nl^N n_1 l_1^{N_1}$ and $nl^N n_1 l_1^{N_1} n_2 l_2$ configurations were studied. In this paper we consider one-electron core excitations for and between the configurations under study. This work combined with Part II and III is a complete description of an electrostatic interaction. In Part I we presented a method which allows to analyse complex electronic systems. They constitute the basis for the design of an efficient computer program package allowing large scale calculations which provide accurate wave functions.

1 Introduction

This paper is the fourth in the series on *Construction of the energy matrix for complex atoms*. In the first work [1] we introduced in general terms a method allowing the analysis of a complex electronic system composed of a configuration of up to four open shells, taking into account all electromagnetic interactions expected in an atom. As it is well known, the construction of an energy matrix is not possible on the infinite basis. Therefore, the wavefunctions corresponding to the atomic energy states are expanded in the broadest system of possible interacting configurations. On this basis, the energy matrix of the Hamiltonian [2–5] describing the fine structure of an atom is constructed, accounting for the interactions up to the first order of the perturbation theory. The calculation details of the matrix elements of the particular Hamiltonian constituents were discussed, and the formulae were presented in our earlier works [6,7]. In these works we laid a particular stress on $(n\mathrm{d}+n'\mathrm{s})^{N+2}+n\mathrm{d}^N n_1 l_1 n_2 l_2$ configurations. In the analysis of the spectra of complex atoms, such as europium, praseodymium or tantalum, there appear electrostatic interactions between many types of configurations involving up to four open electronic shells. In this case, constructing the energy matrix is more complex than in the case previously described in [6,7]. In our second paper of the above-mentioned series [8], those missing interactions were added. 36 new formulae for the first-order electrostatic interaction between configurations up to four open shells were presented.

However, even though many interacting configurations were included, the perturbations produced by all the weakly interacting configurations remained. In spite of the fact that a correction from a single distant perturbing configuration is rather small, their cumulative influence may be considerable, due to the increasing density of states as the continuum is approached. The second-order effects, so-called configuration interaction effects (C), are observed both in the fine- and hyperfine-structure study. Therefore, our energy matrix is extended by the elements comprising electrostatic coupling and electrostatically correlated spin-orbit coupling between the configurations of the system considered and the distant configurations. Generally, for the configurations containing up to three open electronic shells, these matrix

[a] e-mail: magdalena.elantkowska@put.poznan.pl

elements originate from the second-order perturbation theory and can be schematically expressed as follows:

$$\mathrm{C} = -\sum_{\psi''\neq\psi,\psi'} \left[\langle\psi|\mathbf{G}|\psi''\rangle \times \langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E = -(\text{angular part}) \times (\text{radial part}) \qquad (1)$$

and electrostatically correlated spin-orbit interactions (CSO) are defined as follows:

$$\mathrm{CSO} = -\sum_{\psi''\neq\psi,\psi'} \left[\langle\psi|\mathbf{G}|\psi''\rangle \times \langle\psi''|\mathbf{H}_{\mathrm{so}}|\psi'\rangle + \langle\psi|\mathbf{H}_{\mathrm{so}}|\psi''\rangle \times \langle\psi''|\mathbf{G}|\psi'\rangle\right]/\Delta E = -(\text{angular part}) \times (\text{radial part}), \qquad (2)$$

where ψ, ψ' represent particular states of the considered system configurations, ψ'' denote all perturbing virtual states included in our system, $\mathbf{G}$ denotes the two-body operator of an electrostatic interaction, $\mathbf{H}_{\mathrm{so}}$ denotes the one-body operator of a spin-orbit interaction, and ΔE denotes the energy difference between the centre of gravity of the considered configuration and the particular perturbing configuration.

In the third part [9] of our series we started discussing the second-order electrostatic effects, namely we concentrated on the excitation of two equivalent electrons from a closed shell into an open shell or into an empty shell. The current paper concerns the effects of one electron excitation from a closed shell into an open shell.

2 The description of configuration interaction effects

A correction of the form $\alpha L(L+1)$ was first introduced intuitively to the Slater formulae for the energy levels by Tress [10–12], which resulted in a greatly improved agreement between theoretical and experimental values. The first comprehensive analysis of the second-order electrostatic interaction was made by Rajnak, Wyoburne and Judd [13–16], who defined the relevant effective operators, which do not constitute real physical interactions but rather serve as a mathematical tool which allows to include the higher order perturbations. In the above-mentioned papers, it was shown that the second-order electrostatic interaction configurations l^N with distant configurations should be represented by two kinds of effective operators: the two-body ones, so-called two-electron excitation, and the three-body ones, so-called one-electron excitation. According to [13–16], the effects of two-electron excitations can be included in the consideration by effective operators, for which the eigenvalues are: $\alpha L(L+1)$ for p^N configuration, $\alpha L(L+1) + \beta G(R_5)$ for d^N configuration, and $\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7)$ for f^N configuration. $G(R_5)$, $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operators for the group R_5, G_2 and R_7, respectively, and α, β, γ represent the radial part of operators.

A clear description of the effective electrostatic interaction for the configuration system $(l+l')^{N+2}$ with particular emphasis on the $(n\mathrm{d}+n'\mathrm{s})^{N+2}$ type of configurations was given by Feneuille [17–20]. His formalism is based consistently on group theory and comprises both the first- and the second-order perturbation theory. The first application of Feneuille's theory for $(n\mathrm{d}+n'\mathrm{s})^{N+2}$ configurations was sketched by our group in [21], but the two-body and three-body effective operators involved solely d-electrons. Following Feneuille's considerations, we utilized some of his ideas in our paper [6] concerning the construction of the energy matrix for the $(n\mathrm{d}+n'\mathrm{s})^{N+2} + n\mathrm{d}^N n_1 l_1 n_2 l_2$ space of configurations. For the above configuration space we provided a comprehensive analysis of the two-electron operators and three-electron operators describing the interaction involving only d- and s-electrons. We presented the formulae for calculating the relevant matrix elements. The method presented by the above-mentioned paper [6] was applied to the interpretation of the fine structure of the first spectrum of Fe, V, Ti and Co atoms [22–25]. Unfortunately, no paper exists in which effective electrostatic interactions (C) are described for electronic systems composed of more complex configurations. We substituted the description of the configuration interaction through effective operators with direct expression of the above-mentioned effects.

In the work of 2010 [26] we presented our new method. We considered the configuration system $(5\mathrm{d}+6\mathrm{s})^N$ of the lanthanum atom, which is well isolated from any disturbing configurations, and the conditions for the application of the perturbation theory are fulfilled. It yields an excellent possibility of an alternative analysis of the contributions mentioned within the second-order perturbation theory according to the excitation model, either "open shell - empty shell" or "closed shell - open shell". A simultaneous application of both models is not possible due to the fact that in both models an implicit linear dependence between angular coefficients corresponding to certain radial parameters has to occur, which makes the solution of a redundant set of linear equations impossible, thus hindering the determination of the respective radial parameters. It provides an excellent test confirming the correctness of the complex formulae derived, *e.g.* for the configurations with three open shells, which require recoupling of five or more angular momenta and strict observance of the electron permutation rules, in particular for interconfiguration matrix elements.

In summary, on the basis of our considerations included in [26] we suggest considering the broadest possible basis of configurations in the first-order of the perturbation theory, while the second-order effects of the perturbation theory should be described by both the excitation of two electrons from a closed shell to an open shell or an empty shell and the excitation of one electron from a closed shell to an open shell or an empty shell. Recently, we have presented [9] the appropriate formulae describing the excitation of two electrons from a closed shell to an open shell for the following configurations: nl^N, $nl^N n_1 l_1^{N_1}$, $nl^N n_1 l_1^{N_1} n_2 l_2$ and $nl^N n_1 l_1 n_2 l_2^{N_2}$, as well as between the configurations.

3 A proposal of the description of the excitation of one electron from a closed shell into an open shell or an empty shell

The construction of the energy matrix of the Hamiltonian [2–5, 27] describing the fine structure of an atom requires calculation of numerous integrals dependent on the angular coordinates and various radial integrals. The integrals over angular coordinates can be exactly determined, which is not possible in the case of radial integrals. Therefore, the matrix elements of the Hamiltonian are considered as linear combinations of radial integrals where the angular integrals serve as the coefficients of expansions. The radial integrals are treated as free (or constrained) parameters, which can be determined by fitting the calculated levels to the experimental ones with the least squares method.

In this paper we concentrate on the excitation of one electron from a closed shell into an open shell or into an empty shell for the extended model configuration space. There is no paper in which this excitation is described for other configurations than the nl^N configuration. There are also no works in the literature where the formulae describing the interconfiguration effective electrostatic interaction are presented.

The angular part of the matrix elements of eq. (1), describing the configuration interaction effects, is presented in sect. 5. The radial part of the matrix elements is defined as

$$R^t\left(n_al_an_bl_b, n_cl_cn_dl_d\right) R^{t'}\left(n'_al'_an'_bl'_b, n'_cl'_cn'_dl'_d\right), \tag{3}$$

where R^t and $R^{t'}$ represent the Slater radial integrals, which arise from the radial parts of one-electron eigenfunctions.

The Slater radial integrals R^t are defined by [27]

$$R^t\left(n_al_an_bl_b, n_cl_cn_dl_d\right) = e^2 \int_0^\infty \int_0^\infty \frac{r_<^t}{r_>^{t+1}} R_{n_al_a}(r_1) R_{n_bl_b}(r_2) R_{n_cl_c}(r_1) R_{n_dl_d}(r_2)\, \mathrm{d}r_1 \mathrm{d}r_2, \tag{4}$$

where e is the electron charge, r_1 and r_2 are the coordinates of electrons, $r_<$ and $r_>$ indicate the distances from the nucleus to the closer and more distant electron, respectively.

3.1 $\mathbf{nl^N}$ configuration

For the nl^N configuration, the excitation from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^N shell is described by the radial integral of type $R^t(n_0l_0nl, nlnl)R^{t'}(n_0l_0nl, nlnl)$ (eqs. (11) and (12) in sect. 5.1).

The excitation from a closed $n_0l_0^{4l_0+2}$ shell into an empty n_1l_1 shell needs to be considered for the complete description of one electron excitations in the multiconfiguration approximation. This excitation is expressed by the following radial integrals: $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0nl, n_1l_1nl)$, $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0nl, nln_1l_1)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0nl, n_1l_1nl)$ and $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0nl, nln_1l_1)$ (eqs. (14), (15), (16) and (17) in sect. 5.1). The summation over t and t', also over electrons n_0l_0 from different closed shells, is omitted.

The same parameters exist for the $nl^Nn_1l_1^{N_1}$ configuration, but they are derived from the excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open $n_1l_1^{N_1}$ shell (eqs. (26), (27), (28) and (29) in sect. 5.2).

3.2 $\mathbf{nl^Nn_1l_1^{N_1}}$ configuration

For the $nl^Nn_1l_1^{N_1}$ configuration, the excitation from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^N shell is described by the parameters listed in sect. 3.1 and the following new radial integrals: $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$, $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$, $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$ and $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$ (eqs. (19), (20), (21) and (22) in sect. 5.2).

The excitation from a closed $n_0l_0^{4l_0+2}$ shell into an open $n_1l_1^{N_1}$ shell gives radial integrals: $R^t(n_0l_0n_1l_1, n_1l_1n_1l_1)R^{t'}(n_0l_0n_1l_1, n_1l_1n_1l_1)$ (eqs. (24) and (25) in sect. 5.2), and four parameters listed in sect. 3.1.

As for the configuration nl^N, it is necessary to consider the excitation from a closed $n_0l_0^{4l_0+2}$ shell into an empty n_2l_2 shell described by the following radial integrals: $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0nl, nln_2l_2)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0nl, n_2l_2nl)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0nl, nln_2l_2)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0nl, n_2l_2nl)$, $R^t(n_0l_0n_1l_1, n_1l_1n_2l_2)R^{t'}(n_0l_0n_1l_1, n_1l_1n_2l_2)$, $R^t(n_0l_0n_1l_1, n_1l_1n_2l_2)R^{t'}(n_0l_0n_1l_1, n_2l_2n_1l_1)$, $R^t(n_0l_0n_1l_1, n_2l_2n_1l_1)R^{t'}(n_0l_0n_1l_1, n_1l_1n_2l_2)$ and $R^t(n_0l_0n_1l_1, n_2l_2n_1l_1)R^{t'}(n_0l_0n_1l_1, n_2l_2n_1l_1)$ (eqs. (31), (32), (33), (34), (35), (36), (37) and (38) in sect. 5.2).

These parameters then appear in the $nl^Nn_1l_1^{N_1}n_2l_2$ and $nl^Nn_2l_2n_1l_1^{N_1}$ configurations by the excitation from a closed $n_0l_0^{4l_0+2}$ shell into an open n_2l_2 shell (eqs. (62), (63), (64), (65), (66), (67), (68) and (69) in sect. 5.3).

3.3 $nl^N n_1 l_1^{N_1} n_2 l_2$ and $nl^N n_1 l_1 n_2 l_2^{N_2}$ configurations

For the configurations $nl^N n_1 l_1^{N_1} n_2 l_2$ and $nl^N n_1 l_1 n_2 l_2^{N_2}$, the excitation from a closed $n_0 l_0^{4l_0+2}$ shell into an open nl^N shell is described by the identical parameters listed in sect. 3.2 (eqs. (40), (41), (42) and (43) in sect. 5.3).

Additionally, there are parameters involving the electron from the third open shell n_2l_2: $R^t(n_0l_0n_2l_2, nln_2l_2)R^{t'}(n_0l_0n_2l_2, nln_2l_2)$, $R^t(n_0l_0n_2l_2, nln_2l_2)R^{t'}(n_0l_0n_2l_2, n_2l_2nl)$, $R^t(n_0l_0n_2l_2, n_2l_2nl)R^{t'}(n_0l_0n_2l_2, nln_2l_2)$ and $R^t(n_0l_0n_2l_2, n_2l_2nl)R^{t'}(n_0l_0n_2l_2, n_2l_2nl)$ (eqs. (44), (45), (46) and (47) in sect. 5.3).

The excitation from a closed $n_0l_0^{4l_0+2}$ shell into an open $n_1l_1^{N_1}$ shell gives nine types of the radial integrals; five of them are listed in sect. 3.2 (eqs. (49), (50), (51), (52), (53) and (54) in sect. 5.3), four new ones are presented below: $R^t(n_0l_0n_2l_2, n_1l_1n_2l_2)R^{t'}(n_0l_0n_2l_2, n_1l_1n_2l_2)$, $R^t(n_0l_0n_2l_2, n_1l_1n_2l_2)R^{t'}(n_0l_0n_2l_2, n_2l_2n_1l_1)$, $R^t(n_0l_0n_2l_2, n_2l_2n_1l_1)R^{t'}(n_0l_0n_2l_2, n_1l_1n_2l_2)$ and $R^t(n_0l_0n_2l_2, n_2l_2n_1l_1)R^{t'}(n_0l_0n_2l_2, n_2l_2n_1l_1)$ (eqs. (55), (56), (57) and (58) in sect. 5.3).

The excitation from a closed $n_0l_0^{4l_0+2}$ shell into an open n_2l_2 shell gives nine types of the radial integrals; eight of them are listed in sect. 3.2, and the new one is of the form: $R^t(n_0l_0n_2l_2, n_2l_2n_2l_2)R^{t'}(n_0l_0n_2l_2, n_2l_2n_2l_2)$ (eqs. (60) and (61) in sect. 5.3).

For the configurations in this section it is not necessary to consider the excitation from the closed $n_0l_0^{4l_0+2}$ shell into the empty n_3l_3 shell because in a real atom, such configurations rarely exist.

3.4 Inter-configuration parameters

In order to more clearly present our method, we give the example of calculations on Th^+ which were carried out recently [28]. In this study we consider the system of 70 even configurations:

$$\sum_{n'=6}^{11} 5f^2n'd + \sum_{n'=7}^{11} 5f^2n's + \sum_{n'=5}^{9} 5f^2n'g + \sum_{n'=7}^{11} 5f\ 6dn'p + 5f\ 6d6f + \sum_{n'=7}^{11} 5f\ 7sn'p + 5f\ 6f7s + 6d^3 + \sum_{n'=7}^{11} 6d^2n's$$
$$+ \sum_{n'=7}^{11} 6d^2n'd + \sum_{n'=5}^{9} 6d^2n'g + 6d\ 7s^2 + \sum_{n'=8}^{11} 6d\ 7sn's + \sum_{n'=7}^{11} 6d7sn'd + \sum_{n'=5}^{9} 6d7sn'g + 6d\ 7p^2 + 7s\ 7p^2 + \sum_{n'=8}^{11} 7s^2n's$$
$$+ \sum_{n'=7}^{11} 7s^2n'd.$$

We take into account all the possible interactions between configurations under study. The configuration interaction between nl^N and $nl^{N-1}n_1l_1$ occurs via a virtual $n_0l_0^{4l_0+1}nl^Nn_1l_1$ configuration. This effect is described by six radial parameters: $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0nl, nlnl)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0nl, nlnl)$, $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$, $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$ and $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$ (eqs. (71), (72), (73), (74) and (75) in sect. 5.5).

The configuration interaction between nl^N and $nl^{N-2}n_1l_1^2$ or $nl^{N-2}n_1l_1n_2l_2$ occurs via a virtual $n_0l_0^{4l_0+1}nl^Nn_1l_1$ configuration. This effect is expressed by four radial parameters: $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(nlnl, n_0l_0n_1l_1)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(nlnl, n_0l_0n_1l_1)$ or $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(nlnl, n_0l_0n_2l_2)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(nlnl, n_0l_0n_2l_2)$ (eqs. (77), (78), (79) and (80) in sect. 5.5).

Between configurations $nl^{N-1}n_1l_1$ and $nl^{N-1}n_2l_2$, we consider the interaction via virtual $n_0l_0^{4l_0+1}nl^Nn_1l_1$ or $n_0l_0^{4l_0+1}nl^{N-1}n_1l_1n_2l_2$ configurations. This effect is described by fourteen radial parameters. The first six parameters are as follows: $R^t(n_0l_0nl, nlnl)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$, $R^t(n_0l_0nl, nlnl)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$, $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$ or $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$, $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$, $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$ (eqs. (82), (83), (84), (85) and (86) in sect. 5.5).

The above parameters also occur in the interaction between configurations $nl^{N-1}n_1l_1n_3l_3$ and $nl^{N-1}n_2l_2n_3l_3$, or between configurations $nl^{N-1}n_3l_3n_1l_1$ and $nl^{N-1}n_3l_3n_2l_2$; for example, between $6d^28s$ and $6d^27d$ and also between 6d7s8s and 6d7s7d (eqs. (130), (131), (132), (133) and (134) in sect. 5.5).

The excitation of one electron from a closed shell to an empty n_2l_2 shell gives next eight parameters: $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0nl, n_1l_1nl)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0nl, nln_1l_1)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0nl, n_1l_1nl)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0nl, nln_1l_1)$, $R^t(n_0l_0n_1l_1, n_2l_2n_1l_1)R^{t'}(n_0l_0n_2l_2, n_1l_1n_2l_2)$,

$R^t(n_0l_0n_1l_1, n_2l_2n_1l_1)R^{t'}(n_0l_0n_2l_2, n_2l_2n_1l_1)$, $R^t(n_0l_0n_1l_1, n_1l_1n_2l_2)R^{t'}(n_0l_0n_2l_2, n_1l_1n_2l_2)$ and $R^t(n_0l_0n_1l_1, n_1l_1n_2l_2)R^{t'}(n_0l_0n_2l_2, n_2l_2n_1l_1)$ (eqs. (88), (89), (90), (91), (92), (93), (94) and (95) in sect. 5.5).

Between the configurations $nl^{N-1}n_1l_1$ and $nl^{N-2}n_1l_1^2$, we consider the interaction via a virtual $n_0l_0^{4l_0+1}nl^Nn_1l_1$, which gives one parameter $R^t(n_0l_0nl, nlnl)R^{t'}(nlnl, n_0l_0n_1l_1)$ (eq. (97) and (98)). The same parameter denotes the interaction between the configurations $nl^Nn_1l_1n_2l_2$ and $nl^{N-1}n_1l_1^2n_2l_2$ (eqs. (136) and (141) in sect. 5.5); for example, between 6d^{2}7s and 6d7s^2 or 6d7s8s and 6d^{0}7s^{2}8s (6d7s7d and 6d^{0}7s^{2}7d).

Between the configurations $nl^{N-1}n_1l_1$ and $nl^{N-2}n_2l_2^2$, we consider the interaction via virtual states from the configuration $n_0l_0^{4l_0+1}nl^{N-1}n_1l_1n_2l_2$. From the viewpoint of configuration $nl^{N-1}n_1l_1$, the excitation of one electron from a closed shell to an empty n_2l_2 shell, gives the next eight parameters: $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$, $R^t(n_0l_0n_1l_1, n_1l_1n_2l_2)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$, $R^t(n_0l_0n_1l_1, n_1l_1n_2l_2)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$, $R^t(n_0l_0n_1l_1, n_2l_2n_1l_1)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$ and $R^t(n_0l_0n_1l_1, n_2l_2n_1l_1)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$ (eqs. (100), (101), (102), (103), (104) and (105) in sect. 5.5).

The same eight parameters are used for the interaction between configurations $nl^Nn_3l_3n_1l_1$ and $nl^{N-1}n_3l_3n_2l_2^2$ (eqs. (166), (167), (168), (169), (170) and (171) in sect. 5.5); for example, between 6d^{2}7d and 6d7p^2 or 6d7s7d and 6d^{0}7s7p^2.

Between the configurations $nl^{N-1}n_1l_1$ and $nl^{N-2}n_2l_2n_1l_1$ (or $nl^{N-2}n_1l_1n_2l_2$,) we consider interaction via a virtual configuration $n_0l_0^{4l_0+1}nl^Nn_1l_1$, which gives three parameters: $R^t(n_0l_0nl, nlnl)R^{t'}(nlnl, n_0l_0n_2l_2)$, $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(nlnl, n_0l_0n_2l_2)$ and $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(nlnl, n_0l_0n_2l_2)$ (eqs. (107), (108), (109) and (110) in sect. 5.5), and via virtual configuration $n_0l_0^{4l_0+1}nl^{N-1}n_1l_1^2$, which gives six parameters: $R^t(n_0l_0n_1l_1, n_1l_1n_1l_1)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$, $R^t(n_0l_0n_1l_1, n_1l_1n_1l_1)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$, $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0n_2l_2, nln_1l_1)$ and $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0n_2l_2, n_1l_1nl)$ (eqs. (112), (113), (114), (115) and (116) in sect. 5.5).

The interaction via virtual configuration $n_0l_0^{4l_0+1}nl^{N-1}n_1l_1n_2l_2$ gives next eight parameters: $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_2l_2, nln_2l_2)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_2l_2, n_2l_2nl)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_2l_2, nln_2l_2)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_2l_2, n_2l_2nl)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$ and $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$ (eqs. (118), (119), (120), (121), (122) and (123) in sect. 5.5).

The same parameters were discussed earlier between configurations nl^N and $nl^{N-1}n_2l_2$; for example, the interaction between 6d^3 and 6d^{2}7s or between 6d^{2}7d and 6d7s7d.

Between the configurations $nl^{N-1}n_1l_1$ and $nl^{N-2}n_2l_2n_3l_3$, we consider the interaction via virtual configuration $n_0l_0^{4l_0+1}nl^{N-1}n_2l_2n_1l_1$, which gives four parameters: $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_3l_3, nln_1l_1)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_3l_3, n_1l_1nl)$ $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_3l_3, nln_1l_1)$ and $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_3l_3, n_1l_1nl)$ (eqs. (125), (126), (127) and (128) in sect. 5.5).

Between the configurations $nl^{N-2}n_1l_1n_3l_3$ and $nl^{N-2}n_2l_2n_3l_3$ (or $nl^{N-2}n_3l_3n_1l_1$ and $nl^{N-2}n_3l_3n_2l_2$), we consider the interaction via virtual configuration $n_0l_0^{4l_0+1}nl^{N-1}n_1l_1n_3l_3$ (or $n_0l_0^{4l_0+1}nl^{N-1}n_3l_3n_1l_1$), which gives six parameters described above in the discussion of the interaction between $nl^{N-1}n_1l_1$ and $nl^{N-1}n_2l_2$ (eqs. (130), (131), (132) and (133) in sect. 5.5).

Between the configurations $nl^Nn_1l_1n_2l_2$ and $nl^{N-1}n_1l_1^2n_2l_2$, we additionally consider the interaction via virtual states which originate from the configuration $n_0l_0^{4l_0+1}nl^{N+1}n_1l_1n_2l_2$, described by four parameters: $R^t(n_0l_0n_2l_2, nln_2l_2)R^{t'}(nlnl, n_0l_0n_1l_1)$, $R^t(n_0l_0n_2l_2, n_2l_2nl)R^{t'}(nlnl, n_0l_0n_1l_1)$, $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(nlnl, n_0l_0n_1l_1)$ and $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(nlnl, n_0l_0n_1l_1)$ (eqs. (137), (138), (139), (140) and (141) in sect. 5.5), and from the other possible virtual configuration $n_0l_0^{4l_0+1}nl^Nn_1l_1^2n_2l_2$, described by 12 parameters: $R^t(n_0l_0n_2l_2, n_1l_1n_2l_2)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$, $R^t(n_0l_0n_2l_2, n_1l_1n_2l_2)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$, $R^t(n_0l_0n_2l_2, n_2l_2n_1l_1)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$, $R^t(n_0l_0n_2l_2, n_2l_2n_1l_1)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$, $R^t(n_0l_0n_1l_1, n_1l_1n_1l_1)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$, $R^t(n_0l_0n_1l_1, n_1l_1n_1l_1)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$, $R^t(n_0l_0n_1l_1, n_1l_1n_1l_1)R^{t'}(n_0l_0n_2l_2, nln_2l_2)$, $R^t(n_0l_0n_1l_1, n_1l_1n_1l_1)R^{t'}(n_0l_0n_2l_2, n_2l_2nl)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0n_1l_1, nln_1l_1)$, $R^t(n_0l_0nl, nln_1l_1)R^{t'}(n_0l_0n_1l_1, n_1l_1nl)$, $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0n_2l_2, nln_2l_2)$ and $R^t(n_0l_0nl, n_1l_1nl)R^{t'}(n_0l_0n_2l_2, n_2l_2nl)$, (eqs. (143), (144), (145), (146), (147), (148), (149), (150) and (151) in sect. 5.5), and from the virtual configuration $n_0l_0^{4l_0+1}nl^Nn_1l_1n_2l_2^2$, described by six parameters: $R^t(n_0l_0n_2l_2, n_2l_2n_2l_2)R^{t'}(n_0l_0n_1l_1, nln_2l_2)$, $R^t(n_0l_0n_2l_2, n_2l_2n_2l_2)R^{t'}(n_0l_0n_1l_1, n_2l_2nl)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_1l_1, nln_2l_2)$, $R^t(n_0l_0nl, nln_2l_2)R^{t'}(n_0l_0n_1l_1, n_2l_2nl)$, $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_1l_1, nln_2l_2)$ and $R^t(n_0l_0nl, n_2l_2nl)R^{t'}(n_0l_0n_1l_1, n_2l_2nl)$, (eqs. (153), (154), (155), (156) and (157) in sect. 5.5).

Between the configurations $nl^N n_1 l_1^2 n_2 l_2$ and $nl^{N+1} n_1 l_1 n_3 l_3$ there exist the interaction via virtual states which originates from the configuration $n_0 l_0^{4l_0+1} nl^{N+1} n_1 l_1^2 n_2 l_2$, described by eight parameters: $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(n_0l_0n_3l_3, n_1l_1n_2l_2)$, $R^t(n_0l_0n_1l_1, nln_1l_1)R^{t'}(n_0l_0n_3l_3, n_2l_2n_1l_1)$, $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(n_0l_0n_3l_3, n_1l_1n_2l_2)$, $R^t(n_0l_0n_1l_1, n_1l_1nl)R^{t'}(n_0l_0n_3l_3, n_2l_2n_1l_1)$, $R^t(n_0l_0n_2l_2, nln_2l_2)R^{t'}(n_0l_0n_3l_3, n_1l_1n_2l_2)$, $R^t(n_0l_0n_2l_2, nln_2l_2)R^{t'}(n_0l_0n_3l_3, n_2l_2n_1l_1)$, $R^t(n_0l_0n_2l_2, n_2l_2nl)R^{t'}(n_0l_0n_3l_3, n_1l_1n_2l_2)$ and $R^t(n_0l_0n_2l_2, n_2l_2nl)R^{t'}(n_0l_0n_3l_3, n_2l_2n_1l_1)$ (eqs. (159), (160), (161), (162), (163) and (164) in sect. 5.5).

For the configurations with the nl^N core, only the excitation from the closed shells $n_0 l_0^{4l_0+2}$ of the same parity should be considered.

In order to verify whether the parameter moves the center of gravity of the configuration only, the normalization procedure of the angular parts of the diagonal matrix elements ($\psi = \psi'$) was introduced according to the following relation:

$$X_{\text{norm}}(SL) = X(SL) - \frac{\sum_{SL}(2S+1)(2L+1)X(SL)}{\sum_{SL}(2S+1)(2L+1)}\,, \tag{5}$$

where $X(SL)$ denotes a matrix element derived directly from the formulae for subsequent SL states. This procedure is similar to the considerations carried out by Rajnak for l^N configuration [13].

The configuration interaction effects were applied by us for the interpretation of the spectra of the lanthanum [26], tantalum [29] and niobium atom [30]. This required the introduction of new formulae, which are presented in this work.

The correctness of the presented formulae was verified by comparing the energy eigenvalues, obtained with our computer program package, to the values generated with the Cowan-code [27,31]. In order to verify the phase relationship, these comparisons were made for the systems of at least three mutually interacting configurations. A direct comparison of the matrix elements was not possible due to the different coupling schemes.

4 Explanation of used symbols

In all the formulae given below, the symbol $\mathbf{G}^t$ denotes a particular term of Coulomb repulsion represented by irreducible tensors of rank t: $\sum_{i>j} r_<^t/r_>^{t+1}(\mathbf{C}_i^t \cdot \mathbf{C}_j^t)$, where $r_<$ and $r_>$ indicate the distances from the nucleus to the closer and more distant electron, respectively. The summation over t is omitted. The expressions describing $\mathbf{G}^t$ element contain coupling schemes used for the derivation of the formula.

For nj-coefficients, one- and two-particle fractional parentage coefficients, the generally accepted notations were used.

The expression $[x, y]$ represents $(2x+1)(2y+1)$. The reduced matrix elements $\mathbf{C}^t$ and $\mathbf{U}^t$ represent

$$(l_1\|\mathbf{C}^t\|l_2) = (-1)^{l_1}\,[(2l_1+1)(2l_2+1)]^{1/2}\begin{pmatrix} l_1 & t & l_2 \\ 0 & 0 & 0 \end{pmatrix} \tag{6}$$

$$\begin{aligned}\left\langle nl^N\alpha_0S_0L_0\left\|\mathbf{U}^t\right\|nl^N\alpha_0'S_0'L_0'\right\rangle &= \delta(S_0,S_0')\;N\;(-1)^{L_0+l+t}\;[L_0,L_0']^{1/2}\\ &\times\sum_{\bar\alpha\bar S\bar L}(-1)^{\bar L}\left(nl^N\alpha_0S_0L_0\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha_0'S_0'L_0'\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\begin{Bmatrix} l & l & t \\ L_0 & L_0' & \bar L \end{Bmatrix}.\end{aligned} \tag{7}$$

The consideration of the configuration with three open shells, where the second and third shell contain up to three electrons, requires the coupling of four angular momenta. Therefore, it is necessary to use $12j$-coefficients, introduced by Jahn and Hoppe [32] and studied by Ord-Smith [33], who found 16 symmetry relations including a convenient new notation. In the comprehensive work of Jucys *et al.* [34], the $12j$-coefficients of this form were referred to as symbols of the first kind. Additionally, Jucys introduced the more convenient symbols of the second kind with 24 symmetry properties and presented a number of useful sum rules on nj-coefficients, which we primarily use in this paper. The most important sum rules, which we used, are described by the formulae: (A 6.13), (A 6.14), (A 6.25), (A 6.26), (A 6.35-6.40) and (A 6.45-6.49) presented in the paper of Jucys *et al.* [34]. Without these sum rules, it would be impossible to write the formulae, presented below in the sect. 5 in such a compressed form. Therefore, the formulae in Jucys's work contain the nj-coefficients of the first kind and of the second kind, so it is convenient to use the following relation between the different type of $12j$-coefficients:

$$\begin{Bmatrix} j_1 & & j_2 & & j_3 & & j_4 & \\ & l_1 & & l_2 & & l_3 & & l_4 \\ k_1 & & k_2 & & k_3 & & k_4 & \end{Bmatrix} = \begin{Bmatrix} l_1 & k_1 & k_2 & k_3 \\ j_1 & l_4 & k_4 & j_3 \\ j_2 & j_4 & l_2 & l_3 \end{Bmatrix}, \tag{8}$$

$$\begin{bmatrix} j_1 & & j_2 & & j_3 & & j_4 & \\ & l_1 & & l_2 & & l_3 & & l_4 \\ k_1 & & k_2 & & k_3 & & k_4 & \end{bmatrix} (-1)^{-j_1+j_2+j_3-j_4+k_1-k_2-k_3+k_4} = \begin{bmatrix} k_3 & j_1 & k_1 & j_2 \\ l_2 & l_1 & l_3 & l_4 \\ k_4 & j_3 & k_2 & j_4 \end{bmatrix}. \tag{9}$$

5 Explicit formulae for configuration interaction effects. Excitation of one electron from a closed shell into an open shell or an empty shell

The formulae for the second-order configuration interaction are presented below.

5.1 $\mathbf{nl^N}$ configuration

The states ψ and ψ' for nl^N configuration are defined as follows:

$$\psi = n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha SL; SL,$$
$$\psi' = n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha' SL; SL.$$

5.1.1 The excitation of one electron from a closed $n_0 l_0^{4l_0+2}$ shell to an open nl^N shell

$$-\sum_{\psi''} \langle \psi |\mathbf{G}| \psi'' \rangle \times \langle \psi'' |\mathbf{G}| \psi' \rangle = -\sum_{\psi''} A(\psi,\psi'') \times C(\psi'',\psi'), \tag{10}$$

where

$$\begin{aligned} A(\psi,\psi'') = {} & N\sqrt{N+1}\,[S'',L'']^{1/2} \sum_{\bar\alpha\bar S\bar L,\hat\alpha\hat S\hat L} (-1)^{2S+3S''+L''+\bar S+\bar L+\hat L+l+l_0+N} \left(nl^N\alpha SL\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \\ & \times \left(nl^{N+1}\alpha''S''L''\{|nl^{N-1}\bar\alpha\bar S\bar L, nl^2\hat\alpha\hat S\hat L\right) [\hat S,\hat L]^{1/2} \begin{Bmatrix} \hat S & \bar S & S'' \\ S & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} \hat L & \bar L & L'' \\ L & l_0 & l \end{Bmatrix} \begin{Bmatrix} l & l_0 & t \\ l & l & \hat L \end{Bmatrix} \\ & \times (l\|\mathbf{C}^t\|l_0)(l\|\mathbf{C}^t\|l) R^t\,(n_0l_0nl, nlnl)\,, \end{aligned} \tag{11}$$

$$\begin{aligned} C(\psi'',\psi') = {} & N\sqrt{N+1}\,[S'',L'']^{1/2} \sum_{\bar\alpha'\bar S'\bar L',\hat\alpha'\hat S'\hat L'} (-1)^{2S+3S''+L''+\bar S'+\bar L'+\hat L'+l+l_0+N} \left(nl^N\alpha' SL\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right) \\ & \times \left(nl^{N+1}\alpha''S''L''\{|nl^{N-1}\bar\alpha'\bar S'\bar L', nl^2\hat\alpha'\hat S'\hat L'\right) [\hat S',\hat L']^{1/2} \begin{Bmatrix} \hat S' & \bar S' & S'' \\ S & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} \hat L' & \bar L' & L'' \\ L & l_0 & l \end{Bmatrix} \begin{Bmatrix} l & l_0 & t' \\ l & l & \hat L' \end{Bmatrix} \\ & \times (l\|\mathbf{C}^{t'}\|l_0)(l\|\mathbf{C}^{t'}\|l) R^{t'}\,(n_0l_0nl, nlnl)\,, \end{aligned} \tag{12}$$

and the perturbing virtual states are defined as $\psi'' = n_0 l_0^{4l_0+1}\ {}^2l_0, nl^{N+1}\alpha''S''L''; SL$.

This parameter occurs for all types of configurations with nl^N core.

5.1.2 The excitation of one electron from a closed $n_0 l_0^{4l_0+2}$ shell into an empty $n_1 l_1$ shell

$$-\sum_{\psi''} \langle \psi |\mathbf{G}| \psi'' \rangle \times \langle \psi'' |\mathbf{G}| \psi' \rangle = -\sum_{\psi''} \left[A(\psi,\psi'') + B(\psi,\psi'')\right] \times \left[C(\psi'',\psi') + D(\psi'',\psi')\right], \tag{13}$$

where

$$A(\psi,\psi'') = \delta(S,S_1'')\ (-1)^{L_1''+L''+l_0+N}\ \frac{[S'',L'']^{1/2}}{[S,L]^{1/2}} \left\langle nl^N\alpha SL\left\|\mathbf{U}^t\right\|nl^N\alpha_1''S_1''L_1''\right\rangle \begin{Bmatrix} l_1 & t & l_0 \\ L & L'' & L_1'' \end{Bmatrix}$$
$$\times\,(l\|\mathbf{C}^t\|l)(l_0\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0nl,n_1l_1nl)\,, \tag{14}$$
$$B(\psi,\psi'') = N\ (-1)^{S+S_1''+l+l_0+N}\ [S_1'',L_1'',S'',L'']^{1/2}\sum_{\bar\alpha\bar S\bar L}\left(nl^N\alpha SL\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right)$$
$$\times\begin{Bmatrix} 1/2 & \bar S & S_1'' \\ 1/2 & S'' & S \end{Bmatrix}\begin{Bmatrix} \bar L & l & L_1'' \\ l & t & l_1 \\ L & l_0 & L'' \end{Bmatrix}(l\|\mathbf{C}^t\|l_1)(l_0\|\mathbf{C}^t\|l)R^t\,(n_0l_0nl,nln_1l_1)\,, \tag{15}$$
$$C(\psi'',\psi') = \delta(S,S_1'')\ (-1)^{L_1''+L''+l_0+N}\ \frac{[S'',L'']^{1/2}}{[S,L]^{1/2}} \left\langle nl^N\alpha' SL\left\|\mathbf{U}^{t'}\right\|nl^N\alpha_1''S_1''L_1''\right\rangle \begin{Bmatrix} l_1 & t' & l_0 \\ L & L'' & L_1'' \end{Bmatrix}$$
$$\times\,(l\|\mathbf{C}^{t'}\|l)(l_0\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(n_0l_0nl,n_1l_1nl)\,, \tag{16}$$
$$D(\psi'',\psi') = N\ (-1)^{S+S_1''+l+l_0+N}\ [S_1'',L_1'',S'',L'']^{1/2}\sum_{\bar\alpha'\bar S'\bar L'}\left(nl^N\alpha' SL\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)$$
$$\times\begin{Bmatrix} 1/2 & \bar S' & S_1'' \\ 1/2 & S'' & S \end{Bmatrix}\begin{Bmatrix} \bar L' & l & L_1'' \\ l & t' & l_1 \\ L & l_0 & L'' \end{Bmatrix}(l\|\mathbf{C}^{t'}\|l_1)(l_0\|\mathbf{C}^{t'}\|l)R^{t'}\,(n_0l_0nl,nln_1l_1)\,, \tag{17}$$

and the perturbing virtual states are defined as $\psi'' = n_0l_0^{4l_0+1}\ {}^2l_0,(nl^N\alpha_1''S_1''L_1'',n_1l_1)S''L'';SL$.

5.2 $nl^N n_1 l_1^{N_1}$ configuration

The states ψ and ψ' for $nl^N n_1 l_1^{N_1}$ configuration are defined as follows:

$$\psi = (n_0l_0^{4l_0+2}\ {}^1S,nl^N\alpha_1S_1L_1)\alpha_1S_1L_1,n_1l_1^{N_1}\alpha_2S_2L_2;SL,$$
$$\psi' = (n_0l_0^{4l_0+2}\ {}^1S,nl^N\alpha_1'S_1'L_1')\alpha_1'S_1'L_1',n_1l_1^{N_1}\alpha_2'S_2'L_2';SL.$$

5.2.1 The excitation of one electron from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^N shell

$$-\sum_{\psi''}\left\langle\psi\left|\mathbf{G}\right|\psi''\right\rangle\times\left\langle\psi''\left|\mathbf{G}\right|\psi'\right\rangle = -\sum_{\psi''}\left[A(\psi,\psi'')+B(\psi,\psi'')\right]\times\left[C(\psi'',\psi')+D(\psi'',\psi')\right], \tag{18}$$

where

$$A(\psi,\psi'') = \delta(S_1,S'')\ \delta(S_2,S_2'')\ \sqrt{N+1}\ (-1)^{L+L_1''+L_2''+l+N}\ \frac{[S_1'',L_1'',L'']^{1/2}}{[S_1]^{1/2}}\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)$$
$$\times\left\langle n_1l_1^{N_1}\alpha_2S_2L_2\left\|\mathbf{U}^t\right\|n_1l_1^{N_1}\alpha_2''S_2''L_2''\right\rangle\begin{Bmatrix} L_2 & L_1 & L \\ L'' & L_2'' & t \end{Bmatrix}\begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1 & t & l \end{Bmatrix}$$
$$\times\,(l_1\|\mathbf{C}^t\|l_1)(l_0\|\mathbf{C}^t\|l)R^t\,(n_0l_0n_1l_1,nln_1l_1)\,, \tag{19}$$
$$B(\psi,\psi'') = N_1\sqrt{N+1}\ (-1)^{2S+S_1+S''+L_2+L_2''+l+l_1+N}\ [S_1'',L_1'',S'',L'',S_2,L_2,S_2'',L_2'']^{1/2}\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)$$
$$\times\sum_{\bar\alpha\bar S\bar L}(-1)^{2\bar S}\left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)\left(n_1l_1^{N_1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)$$
$$\times\begin{Bmatrix} 1/2 & S_1'' & S'' \\ S & S_2'' & \bar S \end{Bmatrix}\begin{Bmatrix} S_2 & S_1 & S \\ S_1'' & \bar S & 1/2 \end{Bmatrix}\begin{bmatrix} L'' & L_1 & l_1 & l_1 \\ L_2'' & l_0 & L_2 & l \\ L & \bar L & L_1'' & t \end{bmatrix}(l_1\|\mathbf{C}^t\|l)(l_0\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0n_1l_1,n_1l_1nl)\,, \tag{20}$$

$$C(\psi'',\psi') = \delta(S_1',S'')\ \delta(S_2',S_2'')\ \sqrt{N+1}\ (-1)^{L+L_1''+L_2''+l+N}\ \frac{[S_1'',L_1'',L'']^{1/2}}{[S_1']^{1/2}}\ \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right)$$
$$\times \left\langle n_1l_1^{N_1}\alpha_2'S_2'L_2' \left\|\mathbf{U}^{t'}\right\| n_1l_1^{N_1}\alpha_2''S_2''L_2''\right\rangle \begin{Bmatrix} L_2' & L_1' & L \\ L'' & L_2'' & t' \end{Bmatrix} \begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1' & t' & l \end{Bmatrix}$$
$$\times (l_1\|\mathbf{C}^{t'}\|l_1)(l_0\|\mathbf{C}^{t'}\|l)R^{t'}\ (n_0l_0n_1l_1,nln_1l_1)\,, \tag{21}$$
$$D(\psi'',\psi') = N_1\sqrt{N+1}\ (-1)^{2S+S_1'+S''+L_2'+L_2''+l+l_1+N}\ [S_1'',L_1'',S'',L'',S_2',L_2',S_2'',L_2'']^{1/2}\ \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right)$$
$$\times \sum_{\bar\alpha'\bar S'\bar L'} (-1)^{2\bar S'}\ \left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)\left(n_1l_1^{N_1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)$$
$$\times \begin{Bmatrix} 1/2 & S_1'' & S'' \\ S & S_2'' & \bar S' \end{Bmatrix} \begin{Bmatrix} S_2' & S_1' & S \\ S_1'' & \bar S' & 1/2 \end{Bmatrix} \begin{bmatrix} L'' & L_1' & l_1 & l_1 \\ L_2'' & l_0 & L_2' & l \\ L & \bar L' & L_1'' & t' \end{bmatrix} (l_1\|\mathbf{C}^{t'}\|l)(l_0\|\mathbf{C}^{t'}\|l_1)R^{t'}\ (n_0l_0n_1l_1,n_1l_1nl)\,, \tag{22}$$

and the perturbing virtual states are defined as $\psi'' = (n_0l_0^{4l_0+1}\ {}^2l_0, nl^{N+1}\alpha_1''S_1''L_1'')S''L'', n_1l_1^{N_1}\alpha_2''S_2''L_2''; SL$.

5.2.2 The excitation of one electron from a closed $n_0l_0^{4l_0+2}$ shell to an open $n_1l_1^{N_1}$ shell

$$-\sum_{\psi''}\langle\psi|\mathbf{G}|\psi''\rangle\times\langle\psi''|\mathbf{G}|\psi'\rangle =$$
$$-\sum_{\psi''}\Big(A1(\psi,\psi'')\times C1(\psi'',\psi') + \big[A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C2(\psi'',\psi')+D2(\psi'',\psi')\big]\Big), \tag{23}$$

where

$$A1(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ N_1\sqrt{N_1+1}\ [S'',L'',S_2'',L_2'',S_2,L_2]^{1/2}$$
$$\times \begin{Bmatrix} S'' & 1/2 & S_1'' \\ S_2 & S & S_2'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1'' \\ L_2 & L & L_2'' \end{Bmatrix} \sum_{\bar\alpha\bar S\bar L,\hat\alpha\hat S\hat L} (-1)^{S+L+S''+L''+2S_2+\bar S+\bar L+\hat L+l_0+l_1+N+N_1}\ [\hat S,\hat L]^{1/2}$$
$$\times \left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)\left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L, n_1l_1^2\hat\alpha\hat S\hat L\right)$$
$$\times \begin{Bmatrix} \bar S & 1/2 & S_2 \\ 1/2 & S_2'' & \hat S \end{Bmatrix} \begin{Bmatrix} \bar L & l_1 & L_2 \\ l_0 & L_2'' & \hat L \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & t \\ l_0 & l_1 & \hat L \end{Bmatrix} (l_1\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l_0)R^t\ (n_0l_0n_1l_1,n_1l_1n_1l_1)\,, \tag{24}$$
$$C1(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ N_1\sqrt{N_1+1}\ [S'',L'',S_2'',L_2'',S_2',L_2']^{1/2}$$
$$\times \begin{Bmatrix} S'' & 1/2 & S_1'' \\ S_2' & S & S_2'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1'' \\ L_2' & L & L_2'' \end{Bmatrix} \sum_{\bar\alpha'\bar S'\bar L',\hat\alpha'\hat S'\hat L'} (-1)^{S+L+S''+L''+2S_2'+\bar S'+\bar L'+\hat L'+l_0+l_1+N+N_1}\ [\hat S',\hat L']^{1/2}$$
$$\times \left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)\left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L', n_1l_1^2\hat\alpha'\hat S'\hat L'\right)$$
$$\times \begin{Bmatrix} \bar S' & 1/2 & S_2' \\ 1/2 & S_2'' & \hat S' \end{Bmatrix} \begin{Bmatrix} \bar L' & l_1 & L_2' \\ l_0 & L_2'' & \hat L' \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & t' \\ l_0 & l_1 & \hat L' \end{Bmatrix} (l_1\|\mathbf{C}^{t'}\|l_1)(l_1\|\mathbf{C}^{t'}\|l_0)R^{t'}\ (n_0l_0n_1l_1,n_1l_1n_1l_1)\,, \tag{25}$$
$$A2(\psi,\psi'') = \delta(S_1,S_1'')\ \sqrt{N_1+1}\ (-1)^{S+S_2''+S''+L+L_1+L_2''+l_0+N+N_1}\ \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2S_2L_2\right)$$
$$\times [S_2'',L_2'',S'',L'']^{1/2}\left\langle nl^N\alpha_1S_1L_1\left\|\mathbf{U}^t\right\|nl^N\alpha_1''S_1''L_1''\right\rangle \begin{Bmatrix} S_2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} L_2 & L & L_1 \\ L'' & l_1 & L_2'' \end{Bmatrix} \begin{Bmatrix} L'' & L_1 & l_1 \\ t & l_0 & L_1'' \end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^t\|l_1)(l\|\mathbf{C}^t\|l)R^t\ (n_0l_0nl,n_1l_1nl)\,, \tag{26}$$
$$B2(\psi,\psi'') = \delta(S'',\bar S)\ N\sqrt{N_1+1}\ (-1)^{S+2S_1+S_2''+3S''+L+L_1+L_1''+L_2''+L''+l+l_0+N+N_1}$$
$$\times \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2S_2L_2\right)\frac{[S_1'',L_1'',S_2'',L_2'',S_1,L_1,L'']^{1/2}}{[S'']^{1/2}} \begin{Bmatrix} S_2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} L_2 & L & L_1 \\ L'' & l_1 & L_2'' \end{Bmatrix}$$

$$\times \sum_{\bar{\alpha}\bar{S}\bar{L}} \left(nl^N \alpha_1 S_1 L_1\{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right) \left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)$$

$$\times \begin{Bmatrix} \bar{L} & L_1'' & l \\ l_0 & t & L'' \end{Bmatrix} \begin{Bmatrix} L_1 & L'' & l_1 \\ t & l & \bar{L} \end{Bmatrix} (l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_1) R^t\left(n_0l_0nl, nln_1l_1\right), \tag{27}$$

$$C2(\psi'', \psi') = \delta(S_1', S_1'')\ \sqrt{N_1+1}\ (-1)^{S+S_2''+S''+L+L_1'+L_2''+l_0+N+N_1} \left(n_1 l_1^{N_1+1}\alpha_2'' S_2'' L_2''\{|n_1 l_1^{N_1}\alpha_2' S_2' L_2'\right)$$

$$\times [S_2'', L_2'', S'', L'']^{1/2} \left\langle nl^N \alpha_1' S_1' L_1' \left\| \mathbf{U}^{t'} \right\| nl^N \alpha_1'' S_1'' L_1'' \right\rangle \begin{Bmatrix} S_2' & S & S_1' \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} L_2' & L & L_1' \\ L'' & l_1 & L_2'' \end{Bmatrix} \begin{Bmatrix} L'' & L_1' & l_1 \\ t' & l_0 & L_1'' \end{Bmatrix}$$

$$\times (l_0\|\mathbf{C}^{t'}\|l_1)(l\|\mathbf{C}^{t'}\|l) R^{t'}\left(n_0l_0nl, n_1l_1nl\right), \tag{28}$$

$$D2(\psi'', \psi') = \delta(S'', \bar{S}')\ N\sqrt{N_1+1}\ (-1)^{S+2S_1'+S_2''+3S''+L+L_1'+L_1''+L_2''+L''+l+l_0+N+N_1}$$

$$\times \left(n_1 l_1^{N_1+1}\alpha_2'' S_2'' L_2''\{|n_1 l_1^{N_1}\alpha_2' S_2' L_2'\right) \frac{[S_1'', L_1'', S_2'', L_2'', S_1', L_1', L'']^{1/2}}{[S'']^{1/2}} \begin{Bmatrix} S_2' & S & S_1' \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} L_2' & L & L_1' \\ L'' & l_1 & L_2'' \end{Bmatrix}$$

$$\times \sum_{\bar{\alpha}'\bar{S}'\bar{L}'} \left(nl^N \alpha_1' S_1' L_1'\{|nl^{N-1}\bar{\alpha}'\bar{S}'\bar{L}'\right) \left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar{\alpha}'\bar{S}'\bar{L}'\right)$$

$$\times \begin{Bmatrix} \bar{L}' & L_1'' & l \\ l_0 & t' & L'' \end{Bmatrix} \begin{Bmatrix} L_1' & L'' & l_1 \\ t' & l & \bar{L}' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l\|\mathbf{C}^{t'}\|l_1) R^{t'}\left(n_0l_0nl, nln_1l_1\right), \tag{29}$$

and the perturbing virtual states are defined as $\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^N \alpha_1'' S_1'' L_1'')S''L'', n_1 l_1^{N_1+1}\alpha_2'' S_2'' L_2''; SL$.

5.2.3 The excitation of one electron from a closed $n_0 l_0^{4l_0+2}$ shell into an empty $n_2 l_2$ shell considered only for $N_1 = 1$

The states ψ and ψ' for $nl^N n_1 l_1$ configuration are defined as follows:

$$\psi = (n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha_1 S_1 L_1)\alpha_1 S_1 L_1, n_1 l_1; SL,$$
$$\psi' = (n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha_1' S_1' L_1')\alpha_1' S_1' L_1', n_1 l_1; SL.$$

$$-\sum_{\psi''} \langle\psi\,|\mathbf{G}|\,\psi''\rangle \times \langle\psi''\,|\mathbf{G}|\,\psi'\rangle =$$
$$-\sum_{\psi''}\Big(\big[A1(\psi,\psi'') + B1(\psi,\psi'')\big] \times \big[C1(\psi'',\psi') + D1(\psi'',\psi')\big]$$
$$+ \big[A2(\psi,\psi'') + B2(\psi,\psi'')\big] \times \big[C2(\psi'',\psi') + D2(\psi'',\psi')\big]\Big), \tag{30}$$

where

$$A1(\psi, \psi'') = N\ (-1)^{S+L+S''+L''+S_2''+L_2''+L_1+L_1''+l+l_2+N}\ \frac{[S_1, L_1, S_1'', L_1'', S_2'', L_2'', L'']^{1/2}}{[S'']^{1/2}}$$

$$\times \begin{Bmatrix} 1/2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1 \\ L'' & l_2 & L_2'' \end{Bmatrix} \sum_{\bar{\alpha}\bar{S}\bar{L}} \delta(S'', \bar{S}) \left(nl^N \alpha_1 S_1 L_1\{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right) \left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar{\alpha}\bar{S}\bar{L}\right)$$

$$\times \begin{Bmatrix} \bar{L} & l & L_1 \\ l_2 & L'' & t \end{Bmatrix} \begin{Bmatrix} l & t & l_0 \\ L'' & L_1'' & \bar{L} \end{Bmatrix} (l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_2) R^t\left(n_0l_0nl, nln_2l_2\right), \tag{31}$$

$$B1(\psi,\psi'') = \delta(S_1'',S_1)\ N\ (-1)^{S+L+2S_1+S_2''+L_2''+3S''+l_0+l+N}\ [S'',L'',S_2'',L_2'',L_1,L_1'']^{1/2} \begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1 & l_2 & t \end{Bmatrix}$$
$$\times \begin{Bmatrix} 1/2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1 \\ L'' & l_2 & L_2'' \end{Bmatrix} \sum_{\bar\alpha\bar S\bar L} (-1)^{\bar L} \left(nl^N\alpha_1 S_1 L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \left(nl^N\alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right)$$
$$\times \begin{Bmatrix} t & l & l \\ \bar L & L_1 & L_1'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_2)(l\|\mathbf{C}^t\|l) R^t\,(n_0l_0nl, n_2l_2nl)\,, \tag{32}$$

$$C1(\psi'',\psi') = N\ (-1)^{S+L+S''+L''+S_2''+L_2''+L_1'+L_1''+l+l_2+N}\ \frac{[S_1',L_1',S_1'',L_1'',S_2'',L_2'',L'']^{1/2}}{[S'']^{1/2}}$$
$$\times \begin{Bmatrix} 1/2 & S & S_1' \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1' \\ L'' & l_2 & L_2'' \end{Bmatrix} \sum_{\bar\alpha'\bar S'\bar L'} \delta(S'',\bar S') \left(nl^N\alpha_1' S_1' L_1'\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right) \left(nl^N\alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)$$
$$\times \begin{Bmatrix} \bar L' & l & L_1' \\ l_2 & L'' & t' \end{Bmatrix} \begin{Bmatrix} l & t' & l_0 \\ L'' & L_1'' & \bar L' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l\|\mathbf{C}^{t'}\|l_2) R^{t'}\,(n_0l_0nl, nln_2l_2)\,, \tag{33}$$

$$D1(\psi'',\psi') = \delta(S_1'',S_1')\ N\ (-1)^{S+L+2S_1'+S_2''+L_2''+3S''+l_0+l+N}\ [S'',L'',S_2'',L_2'',L_1',L_1'']^{1/2} \begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1' & l_2 & t' \end{Bmatrix}$$
$$\times \begin{Bmatrix} 1/2 & S & S_1' \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1' \\ L'' & l_2 & L_2'' \end{Bmatrix} \sum_{\bar\alpha'\bar S'\bar L'} (-1)^{\bar L'} \left(nl^N\alpha_1' S_1' L_1'\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right) \left(nl^N\alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)$$
$$\times \begin{Bmatrix} t' & l & l \\ \bar L' & L_1' & L_1'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l_2)(l\|\mathbf{C}^{t'}\|l) R^{t'}\,(n_0l_0nl, n_2l_2nl)\,, \tag{34}$$

$$A2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ (-1)^{S+L+S''+L''+L_2''+l_0+l_1+N+1}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1 \\ 1/2 & S & S_2'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L'' & l_0 & L_1 \\ l_1 & L & L_2'' \end{Bmatrix} \begin{Bmatrix} l_0 & l_1 & t \\ l_2 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l_2) R^t\,(n_0l_0n_1l_1, n_1l_1n_2l_2)\,, \tag{35}$$

$$B2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ (-1)^{S+L+S''+L''+S_2''+l_0+l_1+N+1}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1 \\ 1/2 & S & S_2'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L'' & l_0 & L_1 \\ l_1 & L & L_2'' \end{Bmatrix} \begin{Bmatrix} l_0 & l_2 & t \\ l_1 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_2)(l_1\|\mathbf{C}^t\|l_1) R^t\,(n_0l_0n_1l_1, n_2l_2n_1l_1)\,, \tag{36}$$

$$C2(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ (-1)^{S+L+S''+L''+L_2''+l_0+l_1+N+1}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1' \\ 1/2 & S & S_2'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L'' & l_0 & L_1' \\ l_1 & L & L_2'' \end{Bmatrix} \begin{Bmatrix} l_0 & l_1 & t' \\ l_2 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l_1)(l_1\|\mathbf{C}^{t'}\|l_2) R^{t'}\,(n_0l_0n_1l_1, n_1l_1n_2l_2)\,, \tag{37}$$

$$D2(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ (-1)^{S+L+S''+L''+S_2''+l_0+l_1+N+1}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1' \\ 1/2 & S & S_2'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L'' & l_0 & L_1' \\ l_1 & L & L_2'' \end{Bmatrix} \begin{Bmatrix} l_0 & l_2 & t' \\ l_1 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l_2)(l_1\|\mathbf{C}^{t'}\|l_1) R^{t'}\,(n_0l_0n_1l_1, n_2l_2n_1l_1)\,, \tag{38}$$

and the perturbing virtual states are defined as $\psi'' = (n_0l_0^{4l_0+1}\ {}^2l_0, nl^N\alpha_1''S_1''L_1'')S''L'', (n_1l_1, n_2l_2)S_2''L_2''; SL$.

5.3 $\mathbf{nl^N n_1 l_1^{N_1} n_2 l_2}$ configuration

The states ψ and ψ' for $nl^N n_1 l_1^{N_1} n_2 l_2$ configuration are defined as follows:

$$\psi = (n_0l_0^{4l_0+2}\ {}^1S, nl^N\alpha_1S_1L_1)\alpha_1S_1L_1, (n_1l_1^{N_1}\alpha_2S_2L_2, n_2l_2)S_3L_3; SL,$$
$$\psi' = (n_0l_0^{4l_0+2}\ {}^1S, nl^N\alpha_1'S_1'L_1')\alpha_1'S_1'L_1', (n_1l_1^{N_1}\alpha_2'S_2'L_2', n_2l_2)S_3'L_3'; SL.$$

5.3.1 The excitation of one electron from a closed $n_0 l_0^{4l_0+2}$ shell into an open nl^N shell

$$
\begin{aligned}
&-\sum_{\psi''} \langle \psi |\mathbf{G}| \psi'' \rangle \times \langle \psi'' |\mathbf{G}| \psi' \rangle = \\
&-\sum_{\psi''} \Big(\big[A1(\psi,\psi'') + B1(\psi,\psi'')\big] \times \big[C1(\psi'',\psi') + D1(\psi'',\psi')\big] \\
&\quad + \big[A2(\psi,\psi'') + B2(\psi,\psi'')\big] \times \big[C2(\psi'',\psi') + D2(\psi'',\psi')\big]\Big),
\end{aligned} \tag{39}
$$

where

$$
\begin{aligned}
A1(\psi,\psi'') &= \delta(S_1,S'')\ \delta(S_2,S_2'')\ \delta(S_3,S_3'')\ \sqrt{N+1}\ (-1)^{2S_1''+2S_3+2S+L+L_2+L_3+L_1''+L_3''+l_0+l_2+N+1} \\
&\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)\frac{[S_1'',L_1'',L'',L_3,L_3'']^{1/2}}{[S_1]^{1/2}}\left\langle n_1l_1^{N_1}\alpha_2S_2L_2\left\|\mathbf{U}^t\right\|n_1l_1^{N_1}\alpha_2''S_2''L_2''\right\rangle \\
&\times \begin{Bmatrix} L_1 & t & L'' \\ L_3'' & L & L_3 \end{Bmatrix}\begin{Bmatrix} t & L_2 & L_2'' \\ l_2 & L_3'' & L_3 \end{Bmatrix}\begin{Bmatrix} l & L_1 & L_1'' \\ L'' & l_0 & t \end{Bmatrix}(l_1\|\mathbf{C}^t\|l_1)(l_0\|\mathbf{C}^t\|l)R^t\left(n_0l_0n_1l_1,nln_1l_1\right),
\end{aligned} \tag{40}
$$

$$
\begin{aligned}
B1(\psi,\psi'') &= N_1\sqrt{N+1}\ (-1)^{2S''+2S_1+3S_3+S_3''+L_1+L_2+L_2''+L''+l+l_1+N+1} \\
&\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)[S_1'',L_1'',S'',L'',S_2,L_2,S_2'',L_2'',S_3,L_3,S_3'',L_3'']^{1/2} \\
&\times \sum_{\bar\alpha\bar S\bar L}\left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)\left(n_1l_1^{N_1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right) \\
&\times \begin{bmatrix} S_3 & 1/2 & S_3'' & 1/2 \\ 1/2 & S & \bar S & S_1'' \\ S_2 & S_2'' & S_1 & S'' \end{bmatrix}\begin{bmatrix} L_1 & L_3 & L_2 & l_1 & l \\ L & l_2 & \bar L & t & L_1'' \\ L'' & L_3'' & L_2'' & l_1 & l_0 \end{bmatrix}(l_1\|\mathbf{C}^t\|l)(l_0\|\mathbf{C}^t\|l_1)R^t\left(n_0l_0n_1l_1,n_1l_1nl\right),
\end{aligned} \tag{41}
$$

$$
\begin{aligned}
C1(\psi'',\psi') &= \delta(S_1',S'')\ \delta(S_2',S_2'')\ \delta(S_3',S_3'')\ \sqrt{N+1}\ (-1)^{2S_1''+2S_3'+2S+L+L_2'+L_3'+L_1''+L_3''+l_0+l_2+N+1} \\
&\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right)\frac{[S_1'',L_1'',L'',L_3',L_3'']^{1/2}}{[S_1']^{1/2}}\left\langle n_1l_1^{N_1}\alpha_2'S_2'L_2'\left\|\mathbf{U}^{t'}\right\|n_1l_1^{N_1}\alpha_2''S_2''L_2''\right\rangle \\
&\times \begin{Bmatrix} L_1' & t' & L'' \\ L_3'' & L & L_3' \end{Bmatrix}\begin{Bmatrix} t' & L_2' & L_2'' \\ l_2 & L_3'' & L_3' \end{Bmatrix}\begin{Bmatrix} l & L_1' & L_1'' \\ L'' & l_0 & t' \end{Bmatrix}(l_1\|\mathbf{C}^{t'}\|l_1)(l_0\|\mathbf{C}^{t'}\|l)R^{t'}\left(n_0l_0n_1l_1,nln_1l_1\right),
\end{aligned} \tag{42}
$$

$$
\begin{aligned}
D1(\psi'',\psi') &= N_1\sqrt{N+1}\ (-1)^{2S''+2S_1'+3S_3'+S_3''+L_1'+L_2'+L_2''+L''+l+l_1+N+1} \\
&\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right)[S_1'',L_1'',S'',L'',S_2',L_2',S_2'',L_2'',S_3',L_3',S_3'',L_3'']^{1/2} \\
&\times \sum_{\bar\alpha'\bar S'\bar L'}\left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)\left(n_1l_1^{N_1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right) \\
&\times \begin{bmatrix} S_3' & 1/2 & S_3'' & 1/2 \\ 1/2 & S & \bar S' & S_1'' \\ S_2' & S_2'' & S_1' & S'' \end{bmatrix}\begin{bmatrix} L_1' & L_3' & L_2' & l_1 & l \\ L & l_2 & \bar L' & t' & L_1'' \\ L'' & L_3'' & L_2'' & l_1 & l_0 \end{bmatrix}(l_1\|\mathbf{C}^{t'}\|l)(l_0\|\mathbf{C}^{t'}\|l_1)R^{t'}\left(n_0l_0n_1l_1,n_1l_1nl\right),
\end{aligned} \tag{43}
$$

$$
\begin{aligned}
A2(\psi,\psi'') &= \delta(S_1,S'')\ \delta(\alpha_2S_2L_2,\alpha_2''S_2''L_2'')\ \delta(S_3,S_3'')\ \sqrt{N+1}\ (-1)^{L+L_2+L_1''+l+l_2+N} \\
&\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)\frac{[S_1'',L_1'',L'',L_3,L_3'']^{1/2}}{[S_1]^{1/2}}\begin{Bmatrix} L_1 & t & L'' \\ L_3'' & L & L_3 \end{Bmatrix}\begin{Bmatrix} L_3 & L_3'' & t \\ l_2 & l_2 & L_2 \end{Bmatrix} \\
&\times \begin{Bmatrix} l_0 & l & t \\ L_1 & L'' & L_1'' \end{Bmatrix}(l_0\|\mathbf{C}^t\|l)(l_2\|\mathbf{C}^t\|l_2)R^t\left(n_0l_0n_2l_2,nln_2l_2\right),
\end{aligned} \tag{44}
$$

$$
\begin{aligned}
B2(\psi,\psi'') &= \delta(\alpha_2S_2L_2,\alpha_2''S_2''L_2'')\ \sqrt{N+1}\ (-1)^{S''+3S_1+2S_2+3S_3+3S_3''+l_0+l_2+N} \\
&\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)[S_1'',L_1'',S'',L'',S_3,L_3,S_3'',L_3'']^{1/2}\begin{Bmatrix} S_1'' & S'' & 1/2 \\ S_3'' & S_2 & S \end{Bmatrix}\begin{Bmatrix} S_1 & S & S_3 \\ S_2 & 1/2 & S_1'' \end{Bmatrix} \\
&\times \begin{bmatrix} L_3'' & l_0 & L_3 & l \\ L_2 & L & t & L_1'' \\ l_2 & l_2 & L'' & L_1 \end{bmatrix}(l_0\|\mathbf{C}^t\|l_2)(l_2\|\mathbf{C}^t\|l)R^t\left(n_0l_0n_2l_2,n_2l_2nl\right),
\end{aligned} \tag{45}
$$

$$C2(\psi'',\psi') = \delta(S_1',S'')\ \delta(\alpha_2'S_2'L_2',\alpha_2''S_2''L_2'')\ \delta(S_3',S_3'')\ \sqrt{N+1}\ (-1)^{L+L_2'+L_1''+l+l_2+N}$$
$$\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right) \frac{[S_1'',L_1'',L'',L_3',L_3'']^{1/2}}{[S_1']^{1/2}} \begin{Bmatrix} L_1' & t' & L'' \\ L_3'' & L & L_3' \end{Bmatrix} \begin{Bmatrix} L_3' & L_3'' & t' \\ l_2 & l_2 & L_2' \end{Bmatrix}$$
$$\times \begin{Bmatrix} l_0 & l & t' \\ L_1' & L'' & L_1'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l_2\|\mathbf{C}^{t'}\|l_2)R^{t'}\,(n_0l_0n_2l_2,nln_2l_2)\,, \tag{46}$$
$$D2(\psi'',\psi') = \delta(\alpha_2'S_2'L_2',\alpha_2''S_2''L_2'')\ \sqrt{N+1}\ (-1)^{S''+3S_1'+2S_2'+3S_3'+3S_3''+l_0+l_2+N}$$
$$\times \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right) [S_1'',L_1'',S'',L'',S_3',L_3',S_3'',L_3'']^{1/2} \begin{Bmatrix} S_1'' & S'' & 1/2 \\ S_3'' & S_2' & S \end{Bmatrix} \begin{Bmatrix} S_1' & S & S_3' \\ S_2' & 1/2 & S_1'' \end{Bmatrix}$$
$$\times \begin{bmatrix} L_3'' & l_0 & L_3' & l \\ L_2' & L & t' & L_1'' \\ l_2 & l_2 & L'' & L_1' \end{bmatrix} (l_0\|\mathbf{C}^{t'}\|l_2)(l_2\|\mathbf{C}^{t'}\|l)R^{t'}\,(n_0l_0n_2l_2,n_2l_2nl)\,, \tag{47}$$

and the perturbing virtual states are defined as $\psi''=(n_0l_0^{4l_0+1}\ {}^2l_0, nl^{N+1}\alpha_1''S_1''L_1'')S''L'', (n_1l_1^{N_1}\alpha_2''S_2''L_2'', n_2l_2)S_3''L_3''; SL$.

5.3.2 The excitation of one electron from a closed $n_0l_0^{4l_0+2}$ shell to an open $n_1l_1^{N_1}$ shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle =$$
$$-\sum_{\psi''}\Big(A1(\psi,\psi'')\times C1(\psi'',\psi') + \big[A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C2(\psi'',\psi')+D2(\psi'',\psi')\big]$$
$$+\big[A3(\psi,\psi'')+B3(\psi,\psi'')\big]\times\big[C3(\psi'',\psi')+D3(\psi'',\psi')\big]\Big), \tag{48}$$

where

$$A1(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ N_1\sqrt{N_1+1}\ [S'',L'',S_2'',L_2'',S_3'',L_3'',S_2,L_2,S_3,L_3]^{1/2}$$
$$\times \begin{Bmatrix} S'' & 1/2 & S_1'' \\ S_3 & S & S_3'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1'' \\ L_3 & L & L_3'' \end{Bmatrix} \begin{Bmatrix} S_3 & 1/2 & S_3'' \\ S_2'' & 1/2 & S_2 \end{Bmatrix} \begin{Bmatrix} L_3 & l_0 & L_3'' \\ L_2'' & l_2 & L_2 \end{Bmatrix}$$
$$\times \sum_{\bar\alpha\bar S\bar L,\hat\alpha\hat S\hat L} (-1)^{S+L+S''+L''+3S_3''+2S_2+3S_3+L_3+L_3''+\bar S+\bar L+\hat L+l_1+l_2+N+N_1}\ [\hat S,\hat L]^{1/2}$$
$$\times \left(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\right)\left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L, n_1l_1^2\hat\alpha\hat S\hat L\right)$$
$$\times \begin{Bmatrix} \bar S & 1/2 & S_2 \\ 1/2 & S_2'' & \hat S \end{Bmatrix} \begin{Bmatrix} \bar L & l_1 & L_2 \\ l_0 & L_2'' & \hat L \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & t \\ l_0 & l_1 & \hat L \end{Bmatrix} (l_1\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l_0)R^t\,(n_0l_0n_1l_1,n_1l_1n_1l_1)\,, \tag{49}$$
$$C1(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ N_1\sqrt{N_1+1}\ [S'',L'',S_2'',L_2'',S_3'',L_3'',S_2',L_2',S_3',L_3']^{1/2}$$
$$\times \begin{Bmatrix} S'' & 1/2 & S_1'' \\ S_3' & S & S_3'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1'' \\ L_3' & L & L_3'' \end{Bmatrix} \begin{Bmatrix} S_3' & 1/2 & S_3'' \\ S_2'' & 1/2 & S_2' \end{Bmatrix} \begin{Bmatrix} L_3' & l_0 & L_3'' \\ L_2'' & l_2 & L_2' \end{Bmatrix}$$
$$\times \sum_{\bar\alpha'\bar S'\bar L',\hat\alpha'\hat S'\hat L'} (-1)^{S+L+S''+L''+3S_3''+2S_2'+3S_3'+L_3'+L_3''+\bar S'+\bar L'+\hat L'+l_1+l_2+N+N_1}\ [\hat S',\hat L']^{1/2}$$
$$\times \left(n_1l_1^{N_1}\alpha_2'S_2'L_2'\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L'\right)\left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha'\bar S'\bar L', n_1l_1^2\hat\alpha'\hat S'\hat L'\right)$$
$$\times \begin{Bmatrix} \bar S' & 1/2 & S_2' \\ 1/2 & S_2'' & \hat S' \end{Bmatrix} \begin{Bmatrix} \bar L' & l_1 & L_2' \\ l_0 & L_2'' & \hat L' \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & t' \\ l_0 & l_1 & \hat L' \end{Bmatrix} (l_1\|\mathbf{C}^{t'}\|l_0)(l_1\|\mathbf{C}^{t'}\|l_0)R^{t'}\,(n_0l_0n_1l_1,n_1l_1n_1l_1)\,, \tag{50}$$

$$A2(\psi,\psi'') = \delta(S_1,S_1'')\ N\sqrt{N_1+1}\ (-1)^{2S_1+2S_2+3S_2''+S_3+S+S_3''+3S''+L+L_3+L_2''+L_3''+l+l_2+N+N_1+1}$$
$$\times \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2S_2L_2\right)[S_2'',L_2'',S'',L'',S_3'',L_3'',S_3,L_3,L_1,L_1'']^{1/2}$$
$$\times \begin{Bmatrix}1/2 & S_2 & S_2''\\ 1/2 & S_3'' & S_3\end{Bmatrix}\begin{Bmatrix}l_1 & L_2 & L_2''\\ l_2 & L_3'' & L_3\end{Bmatrix}\begin{Bmatrix}S_3 & S & S_1\\ S'' & 1/2 & S_3''\end{Bmatrix}\begin{Bmatrix}L_3 & L & L_1\\ L'' & l_1 & L_3''\end{Bmatrix}\begin{Bmatrix}l_0 & L_1'' & L''\\ L_1 & l_1 & t\end{Bmatrix}$$
$$\times \sum_{\bar\alpha\bar S\bar L}(-1)^{\bar L}\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\begin{Bmatrix}t & l & l\\ \bar L & L_1'' & L_1\end{Bmatrix}$$
$$\times (l\|\mathbf{C}^t\|l)(l_0\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0nl,n_1l_1nl)\,, \qquad (51)$$

$$B2(\psi,\psi'') = N\sqrt{N_1+1}\ (-1)^{S+S''+S_3+S_3''+2S_2+3S_2''+L+L_1+L_1''+L_2''+L''+L_3+L_3''+l_0+l+l_1+l_2+N_1+N+1}$$
$$\times \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2S_2L_2\right)\frac{[S_1,L_1,S_1'',L_1'',S_2'',L_2'',S_3,L_3,S_3'',L_3'',L'']^{1/2}}{[S'']^{1/2}}$$
$$\times \begin{Bmatrix}1/2 & S_2 & S_2''\\ 1/2 & S_3'' & S_3\end{Bmatrix}\begin{Bmatrix}l_1 & L_2 & L_2''\\ l_2 & L_3'' & L_3\end{Bmatrix}\begin{Bmatrix}S_3 & S & S_1\\ S'' & 1/2 & S_3''\end{Bmatrix}\begin{Bmatrix}L_3 & L & L_1\\ L'' & l_1 & L_3''\end{Bmatrix}$$
$$\times \sum_{\bar\alpha\bar S\bar L}\delta(\bar S,S'')\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\begin{Bmatrix}\bar L & l & L_1''\\ l_0 & L'' & t\end{Bmatrix}\begin{Bmatrix}l & t & l_1\\ L'' & L_1 & \bar L\end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0nl,nln_1l_1)\,, \qquad (52)$$

$$C2(\psi'',\psi') = \delta(S_1',S_1'')\ N\sqrt{N_1+1}\ (-1)^{2S_1'+2S_2'+3S_2''+S_3'+S+S_3''+3S''+L+L_3'+L_2''+L_3''+l+l_2+N+N_1+1}$$
$$\times \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2'S_2'L_2'\right)[S_2'',L_2'',S'',L'',S_3'',L_3'',S_3',L_3',L_1',L_1'']^{1/2}$$
$$\times \begin{Bmatrix}1/2 & S_2' & S_2''\\ 1/2 & S_3'' & S_3'\end{Bmatrix}\begin{Bmatrix}l_1 & L_2' & L_2''\\ l_2 & L_3'' & L_3'\end{Bmatrix}\begin{Bmatrix}S_3' & S & S_1'\\ S'' & 1/2 & S_3''\end{Bmatrix}\begin{Bmatrix}L_3' & L & L_1'\\ L'' & l_1 & L_3''\end{Bmatrix}\begin{Bmatrix}l_0 & L_1'' & L''\\ L_1' & l_1 & t'\end{Bmatrix}$$
$$\times \sum_{\bar\alpha'\bar S'\bar L'}(-1)^{\bar L'}\left(nl^N\alpha_1'S_1'L_1'\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)\begin{Bmatrix}t' & l & l\\ \bar L' & L_1'' & L_1'\end{Bmatrix}$$
$$\times (l\|\mathbf{C}^{t'}\|l)(l_0\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(n_0l_0nl,n_1l_1nl)\,, \qquad (53)$$

$$D2(\psi'',\psi') = N\sqrt{N_1+1}\ (-1)^{S+S''+S_3'+S_3''+2S_2'+3S_2''+L+L_1'+L_1''+L_2''+L''+L_3'+L_3''+l_0+l+l_1+l_2+N_1+N+1}$$
$$\times \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2'S_2'L_2'\right)\frac{[S_1',L_1',S_1'',L_1'',S_2'',L_2'',S_3',L_3',S_3'',L_3'',L'']^{1/2}}{[S'']^{1/2}}$$
$$\times \begin{Bmatrix}1/2 & S_2' & S_2''\\ 1/2 & S_3'' & S_3'\end{Bmatrix}\begin{Bmatrix}l_1 & L_2' & L_2''\\ l_2 & L_3'' & L_3'\end{Bmatrix}\begin{Bmatrix}S_3' & S & S_1'\\ S'' & 1/2 & S_3''\end{Bmatrix}\begin{Bmatrix}L_3' & L & L_1'\\ L'' & l_1 & L_3''\end{Bmatrix}$$
$$\times \sum_{\bar\alpha'\bar S'\bar L'}\delta(\bar S',S'')\left(nl^N\alpha_1'S_1'L_1'\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha'\bar S'\bar L'\right)\begin{Bmatrix}\bar L' & l & L_1''\\ l_0 & L'' & t'\end{Bmatrix}\begin{Bmatrix}l & t' & l_1\\ L'' & L_1' & \bar L'\end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^{t'}\|l)(l\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(n_0l_0nl,nln_1l_1)\,, \qquad (54)$$

$$A3(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ \sqrt{N_1+1}\ (-1)^{S+2S_2+3S_3+S''+S_2''+S_3''+L_3''+L+L''+N+N_1}$$
$$\times \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2S_2L_2\right)[S_3,L_3,S_3'',L_3'',S'',L'',S_2'',L_2'']^{1/2}\begin{Bmatrix}1/2 & S'' & S_1\\ S & S_3 & S_3''\end{Bmatrix}\begin{Bmatrix}S_2'' & S_3'' & 1/2\\ S_3 & S_2 & 1/2\end{Bmatrix}$$
$$\times \begin{Bmatrix}l_0 & L'' & L_1\\ L & L_3 & L_3''\end{Bmatrix}\begin{Bmatrix}L_3 & l_0 & L_3''\\ L_2 & l_1 & L_2''\\ l_2 & t & l_2\end{Bmatrix}(l_0\|\mathbf{C}^t\|l_1)(l_2\|\mathbf{C}^t\|l_2)R^t\,(n_0l_0n_2l_2,n_1l_1n_2l_2)\,, \qquad (55)$$

$$B3(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ \delta(S_3,S_2'')\ \sqrt{N_1+1}\ (-1)^{3S+S''+2S_1+3S_3''+L+L_2+L_3+L_2''+L''+l_2+l_1+N+N_1}$$
$$\times \left(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2S_2L_2\right)[S_3'',L_3'',S'',L'',L_3,L_2'']^{1/2}\begin{Bmatrix}1/2 & S'' & S_1\\ S & S_2'' & S_3''\end{Bmatrix}\begin{Bmatrix}l_0 & L'' & L_1\\ L & L_3 & L_3''\end{Bmatrix}$$
$$\times \begin{Bmatrix}L_2 & l_2 & L_3\\ t & L_2'' & l_1\end{Bmatrix}\begin{Bmatrix}L_3 & l_0 & L_3''\\ l_2 & L_2'' & t\end{Bmatrix}(l_0\|\mathbf{C}^t\|l_2)(l_2\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0n_2l_2,n_2l_2n_1l_1)\,, \qquad (56)$$

$$C3(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ \sqrt{N_1+1}\ (-1)^{S+2S_2'+3S_3'+S''+S_2''+S_3''+L''+L+L_3''+N+N_1}$$
$$\times \Big(n_1l_1^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2'S_2'L_2'\Big)\ [S_3',L_3',S_3'',L_3'',S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} 1/2 & S'' & S_1' \\ S & S_3' & S_3'' \end{Bmatrix} \begin{Bmatrix} S_2'' & S_3'' & 1/2 \\ S_3' & S_2' & 1/2 \end{Bmatrix}$$
$$\times \begin{Bmatrix} l_0 & L'' & L_1' \\ L & L_3' & L_3'' \end{Bmatrix} \begin{Bmatrix} L_3' & l_0 & L_3'' \\ L_2' & l_1 & L_2'' \\ l_2 & t' & l_2 \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l_2\|\mathbf{C}^{t'}\|l_2)R^{t'}\,(n_0l_0n_2l_2,n_1l_1n_2l_2)\,, \tag{57}$$

$$D3(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ \delta(S_3',S_2'')\ \sqrt{N_1+1}\ (-1)^{3S+S''+2S_1'+3S_3''+L+L_2'+L_3'+L_2''+L''+l_2+l_1+N+N_1}$$
$$\times \Big(n_1l^{N_1+1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1}\alpha_2'S_2'L_2'\Big)\ [S_3'',L_3'',S'',L'',L_3',L_2'']^{1/2} \begin{Bmatrix} 1/2 & S'' & S_1' \\ S & S_2'' & S_3'' \end{Bmatrix} \begin{Bmatrix} l_0 & L'' & L_1' \\ L & L_3' & L_3'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L_2' & l_2 & L_3' \\ t' & L_2'' & l_1 \end{Bmatrix} \begin{Bmatrix} L_3' & l_0 & L_3'' \\ l_2 & L_2'' & t' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l_2)(l_2\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(n_0l_0n_2l_2,n_2l_2n_1l_1)\,, \tag{58}$$

and the perturbing virtual states are defined as $\psi'' = (n_0l_0^{4l_0+1}\ {}^2l_0, nl^N\alpha_1''S_1''L_1'')S''L'', (n_1l_1^{N_1+1}\alpha_2''S_2''L_2'', n_2l_2)S_3''L_3''; SL$.

5.3.3 The excitation of one electron from a closed $n_0l_0^{4l_0+2}$ shell to an open n_2l_2 shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle \times \langle\psi''\,|\mathbf{G}|\,\psi'\rangle =$$
$$-\sum_{\psi''}\Big(A1(\psi,\psi'')\times C1(\psi'',\psi') + \big[A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C2(\psi'',\psi')+D2(\psi'',\psi')\big]$$
$$+\big[A3(\psi,\psi'')+B3(\psi,\psi'')\big]\times\big[C3(\psi'',\psi')+D3(\psi'',\psi')\big]\Big), \tag{59}$$

where

$$A1(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ \delta(\alpha_2S_2L_2,\alpha_2''S_2''L_2'')\ \sqrt{2}\ (-1)^{S+L+3S''+L''+2S_1+S_2+2S_3+L_2+L_4''+N+N_1}$$
$$\times [S'',L'',S_3'',L_3'',S_4'',L_4'',S_3,L_3]^{1/2} \begin{Bmatrix} 1/2 & S_3'' & S_3 \\ S & S_1 & S'' \end{Bmatrix} \begin{Bmatrix} l_0 & L_3'' & L_3 \\ L & L_1 & L'' \end{Bmatrix} \begin{Bmatrix} S_2 & 1/2 & S_3 \\ 1/2 & S_3'' & S_4'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L_2 & l_2 & L_3 \\ l_0 & L_3'' & L_4'' \end{Bmatrix} \begin{Bmatrix} l_2 & l_0 & t \\ l_2 & l_2 & L_4'' \end{Bmatrix} (l_2\|\mathbf{C}^t\|l_2)(l_2\|\mathbf{C}^t\|l_0)R^t\,(n_0l_0n_2l_2,n_2l_2n_2l_2)\,, \tag{60}$$

$$C1(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ \delta(\alpha_2'S_2'L_2',\alpha_2''S_2''L_2'')\ \sqrt{2}\ (-1)^{S+L+3S''+L''+2S_1'+S_2'+2S_3'+L_2'+L_4''+N+N_1}$$
$$\times [S'',L'',S_3'',L_3'',S_4'',L_4'',S_3',L_3']^{1/2} \begin{Bmatrix} 1/2 & S_3'' & S_3' \\ S & S_1' & S'' \end{Bmatrix} \begin{Bmatrix} l_0 & L_3'' & L_3' \\ L & L_1' & L'' \end{Bmatrix} \begin{Bmatrix} S_2' & 1/2 & S_3' \\ 1/2 & S_3'' & S_4'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L_2' & l_2 & L_3' \\ l_0 & L_3'' & L_4'' \end{Bmatrix} \begin{Bmatrix} l_2 & l_0 & t' \\ l_2 & l_2 & L_4'' \end{Bmatrix} (l_2\|\mathbf{C}^{t'}\|l_2)(l_2\|\mathbf{C}^{t'}\|l_0)R^{t'}\,(n_0l_0n_2l_2,n_2l_2n_2l_2)\,, \tag{61}$$

$$A2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ \delta(S_2,S_2'')\ \sqrt{2}N_1\ (-1)^{S+S_2+2S_3+2S_3''+S''+L+L_2+L_3+L_4''+L''+l_0+l_1+N+N_1}$$
$$\times [S_3,L_3,S_3'',L_3'',S'',L'',S_4'',L_4'',L_2,L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1 \\ S_3 & S & S_3'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1 \\ L_3 & L & L_3'' \end{Bmatrix} \begin{Bmatrix} S_2 & 1/2 & S_3 \\ 1/2 & S_3'' & S_4'' \end{Bmatrix} \begin{Bmatrix} L_2'' & L_2 & t \\ L_3'' & L_3 & l_0 \\ L_4'' & l_2 & l_2 \end{Bmatrix}$$
$$\times \sum_{\bar\alpha\bar S\bar L}(-1)^{2\bar S+\bar L}\Big(n_1l_1^{N_1}\alpha_2S_2L_2\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\Big)\Big(n_1l_1^{N_1}\alpha_2''S_2''L_2''\{|n_1l_1^{N_1-1}\bar\alpha\bar S\bar L\Big)$$
$$\times \begin{Bmatrix} L_2'' & L_2 & t \\ l_1 & l_1 & \bar L \end{Bmatrix} (l_1\|\mathbf{C}^t\|l_1)(l_0\|\mathbf{C}^t\|l_2)R^t\,(n_0l_0n_1l_1,n_2l_2n_1l_1)\,, \tag{62}$$

$$
\begin{aligned}
B2(\psi,\psi'') &= \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \sqrt{2} N_1\ [S_2, L_2, S_2'', L_2'', S_3, L_3, S_3'', L_3'', S'', L'', S_4'', L_4'']^{1/2} \\
&\times \begin{Bmatrix} S'' & 1/2 & S_1 \\ S_3 & S & S_3'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1 \\ L_3 & L & L_3'' \end{Bmatrix} \sum_{\bar{\alpha}\bar{S}\bar{L}} \left(n_1 l_1^{N_1} \alpha_2 S_2 L_2 \{| n_1 l_1^{N_1-1} \bar{\alpha}\bar{S}\bar{L}\right) \left(n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'' \{| n_1 l_1^{N_1-1} \bar{\alpha}\bar{S}\bar{L}\right) \\
&\times (-1)^{S+S''+2S_3+3S_3''+2S_2+3S_2''+L+L_2''+L_4''+L''+L_3+3\bar{S}+\bar{L}+N_1+N+3/2} \begin{Bmatrix} S_4'' & \bar{S} & S_3 \\ S_2 & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} S_4'' & \bar{S} & S_3 \\ 1/2 & S_3'' & S_2'' \end{Bmatrix} \\
&\times \begin{Bmatrix} l_1 & t & l_0 & L_3 \\ \bar{L} & l_1 & L_2 & L_4'' \\ L_2'' & l_2 & L_3'' & l_2 \end{Bmatrix} (l_0 \| \mathbf{C}^t \| l)(l_1 \| \mathbf{C}^t \| l_2) R^t\,(n_0 l_0 n_1 l_1, n_1 l_1 n_2 l_2)\,, \qquad (63)
\end{aligned}
$$

$$
\begin{aligned}
C2(\psi'',\psi') &= \delta(\alpha_1' S_1' L_1', \alpha_1'' S_1'' L_1'')\ \delta(S_2', S_2'')\ \sqrt{2} N_1\ (-1)^{S+S_2'+2S_3'+2S_3''+S''+L+L_2'+L_3'+L_4''+L''+l_0+l_1+N+N_1} \\
&\times [S_3', L_3', S_3'', L_3'', S'', L'', S_4'', L_4'', L_2', L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1' \\ S_3' & S & S_3'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1' \\ L_3' & L & L_3'' \end{Bmatrix} \begin{Bmatrix} S_2' & 1/2 & S_3' \\ 1/2 & S_3'' & S_4'' \end{Bmatrix} \begin{Bmatrix} L_2'' & L_2' & t' \\ L_3'' & L_3' & l_0 \\ L_4'' & l_2 & l_2 \end{Bmatrix} \\
&\times \sum_{\bar{\alpha}'\bar{S}'\bar{L}'} (-1)^{2\bar{S}'+\bar{L}'} \left(n_1 l_1^{N_1} \alpha_2' S_2' L_2' \{| n_1 l_1^{N_1-1} \bar{\alpha}'\bar{S}'\bar{L}'\right) \left(n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'' \{| n_1 l_1^{N_1-1} \bar{\alpha}'\bar{S}'\bar{L}'\right) \\
&\times \begin{Bmatrix} L_2'' & L_2' & t' \\ l_1 & l_1 & \bar{L}' \end{Bmatrix} (l_1 \| \mathbf{C}^{t'} \| l_1)(l_0 \| \mathbf{C}^{t'} \| l_2) R^{t'}\,(n_0 l_0 n_1 l_1, n_2 l_2 n_1 l_1)\,, \qquad (64)
\end{aligned}
$$

$$
\begin{aligned}
D2(\psi'',\psi') &= \delta(\alpha_1' S_1' L_1', \alpha_1'' S_1'' L_1'')\ \sqrt{2} N_1\ [S_2', L_2', S_2'', L_2'', S_3', L_3', S_3'', L_3'', S'', L'', S_4'', L_4'']^{1/2} \\
&\times \begin{Bmatrix} S'' & 1/2 & S_1' \\ S_3' & S & S_3'' \end{Bmatrix} \begin{Bmatrix} L'' & l_0 & L_1' \\ L_3' & L & L_3'' \end{Bmatrix} \sum_{\bar{\alpha}'\bar{S}'\bar{L}'} \left(n_1 l_1^{N_1} \alpha_2' S_2' L_2' \{| n_1 l_1^{N_1-1} \bar{\alpha}'\bar{S}'\bar{L}'\right) \left(n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'' \{| n_1 l_1^{N_1-1} \bar{\alpha}'\bar{S}'\bar{L}'\right) \\
&\times (-1)^{S+S''+2S_3'+3S_3''+2S_2'+3S_2''+L+L_2''+L_4''+L''+L_3'+3\bar{S}'+\bar{L}'+N_1+N+3/2} \begin{Bmatrix} S_4'' & \bar{S}' & S_3' \\ S_2' & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} S_4'' & \bar{S}' & S_3' \\ 1/2 & S_3'' & S_2'' \end{Bmatrix} \\
&\times \begin{Bmatrix} l_1 & t' & l_0 & L_3' \\ \bar{L}' & l_1 & L_2' & L_4'' \\ L_2'' & l_2 & L_3'' & l_2 \end{Bmatrix} (l_0 \| \mathbf{C}^{t'} \| l)(l_1 \| \mathbf{C}^{t'} \| l_2) R^{t'}\,(n_0 l_0 n_1 l_1, n_1 l_1 n_2 l_2)\,, \qquad (65)
\end{aligned}
$$

$$
\begin{aligned}
A3(\psi,\psi'') &= \delta(\alpha_2 S_2 L_2, \alpha_2'' S_2'' L_2'')\ \delta(S_1, S_1'')\ \sqrt{2} N\ (-1)^{S+S_2+2S_3+S''+L+L_2+l+l_2+N+N_1+1} \\
&\times [S_3, L_3, S_3'', L_3'', S'', L'', S_4'', L_4'', L_1, L_1'']^{1/2} \begin{Bmatrix} S_3 & S & S_1 \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_3 & L & L_1 \\ L'' & l_2 & L_3'' \end{Bmatrix} \begin{Bmatrix} 1/2 & S_3'' & S_3 \\ S_2 & 1/2 & S_4'' \end{Bmatrix} \begin{Bmatrix} l_2 & L_3'' & L_3 \\ L_2 & l_2 & L_4'' \end{Bmatrix} \\
&\times \begin{Bmatrix} L_1 & L'' & l_2 \\ l_0 & t & L_1'' \end{Bmatrix} \sum_{\bar{\alpha}\bar{S}\bar{L}} (-1)^{\bar{L}} \left(n l^N \alpha_1 S_1 L_1 \{| n l^{N-1} \bar{\alpha}\bar{S}\bar{L}\right) \left(n l^N \alpha_1'' S_1'' L_1'' \{| n l^{N-1} \bar{\alpha}\bar{S}\bar{L}\right) \\
&\times \begin{Bmatrix} \bar{L} & L_1'' & l \\ t & l & L_1 \end{Bmatrix} (l \| \mathbf{C}^t \| l)(l_0 \| \mathbf{C}^t \| l_2) R^t\,(n_0 l_0 n l, n_2 l_2 n l)\,, \qquad (66)
\end{aligned}
$$

$$
\begin{aligned}
B3(\psi,\psi'') &= \delta(\alpha_2 S_2 L_2, \alpha_2'' S_2'' L_2'')\ \sqrt{2} N\ (-1)^{S+S''+2S_1+S_2+3S_3+2S_1''+L+L_1+L_2+L_1''+L''+l+l_0+N_1+N} \\
&\times [S_1, L_1, S_1'', L_1'', S_3, L_3, S_3'', L_3'', L'', S_4'', L_4'']^{1/2} \begin{Bmatrix} S_3 & S & S_1 \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_3 & L & L_1 \\ L'' & l_2 & L_3'' \end{Bmatrix} \begin{Bmatrix} 1/2 & S_3'' & S_3 \\ S_2 & 1/2 & S_4'' \end{Bmatrix} \begin{Bmatrix} l_2 & L_3'' & L_3 \\ L_2 & l_2 & L_4'' \end{Bmatrix} \\
&\times \sum_{\bar{\alpha}\bar{S}\bar{L}} \delta(S'', \bar{S}) [\bar{S}]^{-1/2} \left(n l^N \alpha_1 S_1 L_1 \{| n l^{N-1} \bar{\alpha}\bar{S}\bar{L}\right) \left(n l^N \alpha_1'' S_1'' L_1'' \{| n l^{N-1} \bar{\alpha}\bar{S}\bar{L}\right) \\
&\times \begin{Bmatrix} \bar{L} & L_1'' & l \\ l_0 & t & L'' \end{Bmatrix} \begin{Bmatrix} L_1 & L'' & l_2 \\ t & l & \bar{L} \end{Bmatrix} (l_0 \| \mathbf{C}^t \| l)(l \| \mathbf{C}^t \| l_2) R^t\,(n_0 l_0 n l, n l n_2 l_2)\,, \qquad (67)
\end{aligned}
$$

$$C3(\psi'',\psi') = \delta(\alpha_2' S_2' L_2', \alpha_2'' S_2'' L_2'')\ \delta(S_1', S_1'')\ \sqrt{2}N\ (-1)^{S+S_2'+2S_3'+S''+L+L_2'+l+l_2+N+N_1+1}$$
$$\times [S_3', L_3', S_3'', L_3'', S'', L'', S_4'', L_4'', L_1', L_1'']^{1/2} \begin{Bmatrix} S_3' & S & S_1' \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_3' & L & L_1' \\ L'' & l_2 & L_3'' \end{Bmatrix} \begin{Bmatrix} 1/2 & S_3'' & S_3' \\ S_2' & 1/2 & S_4'' \end{Bmatrix} \begin{Bmatrix} l_2 & L_3'' & L_3' \\ L_2' & l_2 & L_4'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L_1' & L'' & l_2 \\ l_0 & t' & L_1'' \end{Bmatrix} \sum_{\bar{\alpha}'\bar{S}'\bar{L}'} (-1)^{\bar{L}'} \left(nl^N \alpha_1' S_1' L_1' \{| nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}'\right) \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}'\right)$$
$$\times \begin{Bmatrix} \bar{L}' & L_1'' & l \\ t' & l & L_1' \end{Bmatrix} (l\|\mathbf{C}^{t'}\|l)(l_0\|\mathbf{C}^{t'}\|l_2) R^{t'}(n_0l_0nl, n_2l_2nl)\,, \tag{68}$$

$$D3(\psi'',\psi') = \delta(\alpha_2' S_2' L_2', \alpha_2'' S_2'' L_2'')\ \sqrt{2}N\ (-1)^{S+S''+2S_1'+S_2'+3S_3'+2S_1''+L+L_1'+L_2'+L_1''+L''+l+l_0+N_1+N}$$
$$\times [S_1', L_1', S_1'', L_1'', S_3', L_3', S_3'', L_3'', L'', S_4'', L_4'']^{1/2} \begin{Bmatrix} S_3' & S & S_1' \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_3' & L & L_1' \\ L'' & l_2 & L_3'' \end{Bmatrix} \begin{Bmatrix} 1/2 & S_3'' & S_3' \\ S_2' & 1/2 & S_4'' \end{Bmatrix} \begin{Bmatrix} l_2 & L_3'' & L_3' \\ L_2' & l_2 & L_4'' \end{Bmatrix}$$
$$\times \sum_{\bar{\alpha}'\bar{S}'\bar{L}'} \delta(S'', \bar{S}')[\bar{S}']^{-1/2} \left(nl^N \alpha_1' S_1' L_1' \{| nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}'\right) \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1} \bar{\alpha}' \bar{S}' \bar{L}'\right)$$
$$\times \begin{Bmatrix} \bar{L}' & L_1'' & l \\ l_0 & t' & L'' \end{Bmatrix} \begin{Bmatrix} L_1' & L'' & l_2 \\ t' & l & \bar{L}' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l\|\mathbf{C}^{t'}\|l_2) R^{t'}(n_0l_0nl, nln_2l_2)\,, \tag{69}$$

and the perturbing virtual states are defined as

$$\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'', n_2 l_2^2 \alpha_4'' S_4'' L_4'') S_3'' L_3''; SL.$$

5.4 $\mathbf{nl^N n_2 l_2 n_1 l_1^{N_1}}$ configuration

The states ψ and ψ' for $nl^N n_2 l_2 n_1 l_1^{N_1}$ configuration are defined as follows:

$$\psi = (n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha_1 S_1 L_1) \alpha_1 S_1 L_1, (n_2 l_2, n_1 l_1^{N_1} \alpha_2 S_2 L_2) S_3 L_3; SL,$$
$$\psi' = (n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha_1' S_1' L_1') \alpha_1' S_1' L_1', (n_2 l_2, n_1 l_1^{N_1} \alpha_2' S_2' L_2') S_3' L_3'; SL.$$

5.4.1 The excitation of one electron $n_0 l_0$ from a closed $n_0 l_0^{4l_0+2}$ shell to an open nl^N shell

Through the proper recoupling procedures each of the components of the sum in eq. (39) must be multiplied by a phase factor equal to $(-1)^{S_2+L_2+S_2'+L_2'+3S_3+L_3+3S_3'+L_3'+2S_2''+2S_3''}$, and the perturbing virtual states are defined as

$$\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^{N+1} \alpha_1'' S_1'' L_1'') S'' L'', (n_2 l_2, n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'') S_3'' L_3''; SL.$$

5.4.2 The excitation of one electron $n_0 l_0$ from a closed $n_0 l_0^{4l_0+2}$ shell to a partially filled $n_1 l_1^{N_1}$ shell

Through the proper recoupling procedures each of the components of the sum in eq. (48) must be multiplied by a phase factor equal to $(-1)^{S_2+L_2+S_2'+L_2'+3S_3+L_3+3S_3'+L_3'+2S_2''+2S_3''}$, and the perturbing virtual states are defined as

$$\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_2 l_2, n_1 l_1^{N_1+1} \alpha_2'' S_2'' L_2'') S_3'' L_3''; SL.$$

5.4.3 The excitation of one electron from a closed $n_0 l_0^{4l_0+2}$ shell into an open $n_2 l_2$ shell

Through the proper recoupling procedures each of the components of the sum in eq. (59) must be multiplied by a phase factor equal to $(-1)^{S_2+L_2+S_2'+L_2'+3S_3+L_3+3S_3'+L_3'+2S_2''+2S_3''+1}$, and the perturbing virtual states are defined as

$$\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_2 l_2^2\ \alpha_4'' S_4'' L_4'', n_1 l_1^{N_1} \alpha_2'' S_2'' L_2'') S_3'' L_3''; SL.$$

5.5 Inter-configuration matrix elements

5.5.1 The configuration interaction $nl^N \leftrightarrow nl^{N-1}n_1l_1$

The states ψ for nl^N configuration and ψ' for $nl^{N-1}n_1l_1$ configuration are defined as follows:

$$\psi = n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha SL; SL,$$
$$\psi' = n_0 l_0^{4l_0+2}\ {}^1S, (nl^{N-1}\alpha_1' S_1' L_1', n_1 l_1) SL; SL.$$

The excitation of an electron from a closed $n_0 l_0^{4l_0+2}$ shell into an open nl^{N-1} shell

$$-\sum_{\psi''} \langle \psi |\mathbf{G}| \psi'' \rangle \times \langle \psi'' |\mathbf{G}| \psi' \rangle = -\sum_{\psi''} \big[A(\psi,\psi'') + B(\psi,\psi'')\big] \times \big[C1(\psi'',\psi') + C2(\psi'',\psi') + D2(\psi'',\psi')\big], \tag{70}$$

where

$$A(\psi,\psi'') = \delta(S,S_1'')(-1)^{L''+L_1''+l_1+N}\ \frac{[S'',L'']^{1/2}}{[S,L]^{1/2}} \left\langle nl^N\alpha SL \left\| \mathbf{U}^t \right\| nl^N \alpha_1'' S_1'' L_1'' \right\rangle \begin{Bmatrix} l_0 & t & l_1 \\ L_1'' & L'' & L \end{Bmatrix}$$
$$\times (l\|\mathbf{C}^t\|l)(l_1\|\mathbf{C}^t\|l_0) R^t\left(n_0 l_0 nl, n_1 l_1 nl\right), \tag{71}$$

$$B(\psi,\psi'') = N\ (-1)^{S+S_1''+l+l_1+N}\ [S'',L'',S_1'',L_1'']^{1/2} \sum_{\bar\alpha \bar S \bar L} \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1}\bar\alpha \bar S \bar L\right) \left(nl^N \alpha SL \{| nl^{N-1}\bar\alpha \bar S \bar L\right)$$
$$\times \begin{Bmatrix} 1/2 & \bar S & S \\ 1/2 & S'' & S_1'' \end{Bmatrix} \begin{Bmatrix} \bar L & l & L \\ l & t & l_0 \\ L_1'' & l_1 & L'' \end{Bmatrix} (l\|\mathbf{C}^t\|l_0)(l_1\|\mathbf{C}^t\|l) R^t\left(n_0 l_0 nl, nl n_1 l_1\right), \tag{72}$$

$$C1(\psi'',\psi') = \delta(S_1',\bar S')\sqrt{N}\ (-1)^{S+S_1''+L+L_1'+l+l_0+l_1+N+1}\ [S'',L'',S_1'',L_1'']^{1/2} \begin{Bmatrix} 1/2 & S & S_1' \\ 1/2 & S_1'' & S'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1' \\ l_0 & L_1'' & L'' \end{Bmatrix}$$
$$\times \sum_{\bar\alpha' \bar S' \bar L'} \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1}\bar\alpha' \bar S' \bar L'\right) \left\langle nl^{N-1}\bar\alpha' \bar S' \bar L' \left\| \mathbf{U}^{t'} \right\| nl^{N-1}\alpha_1' S_1' L_1' \right\rangle \begin{Bmatrix} \bar L' & t' & L_1' \\ l_0 & L_1'' & l \end{Bmatrix}$$
$$\times (l\|\mathbf{C}^{t'}\|l)(l\|\mathbf{C}^{t'}\|l_0) R^{t'}\left(n_0 l_0 nl, nl nl\right), \tag{73}$$

$$C2(\psi'',\psi') = \sqrt{N}\ (-1)^{2S_1'+3S_1''+S+N+1} \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1}\alpha_1' S_1' L_1'\right) [S'',L'',S_1'',L_1'']^{1/2}$$
$$\times \begin{Bmatrix} S_1' & 1/2 & S \\ S'' & 1/2 & S_1'' \end{Bmatrix} \begin{Bmatrix} L'' & l_1 & L_1'' \\ l_0 & t' & l \\ L & l_1 & L_1' \end{Bmatrix} (l_1\|\mathbf{C}^{t'}\|l_1)(l_0\|\mathbf{C}^{t'}\|l) R^{t'}\left(n_0 l_0 n_1 l_1, nl n_1 l_1\right), \tag{74}$$

$$D2(\psi'',\psi') = \delta(S_1'',S)\ \sqrt{N}\ (-1)^{2S_1'+2S+L+L_1'+L''+L_1''+l+l_1+N+1} \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1}\alpha_1' S_1' L_1'\right)$$
$$\times \frac{[S'',L'',L_1'']^{1/2}}{[S]^{1/2}} \begin{Bmatrix} t' & l_0 & l_1 \\ L'' & L_1'' & L \end{Bmatrix} \begin{Bmatrix} L & t' & L_1'' \\ l & L_1' & l_1 \end{Bmatrix} (l_1\|\mathbf{C}^{t'}\|l)(l_0\|\mathbf{C}^{t'}\|l_1) R^{t'}\left(n_0 l_0 n_1 l_1, n_1 l_1 nl\right), \tag{75}$$

and the perturbing virtual states are defined as $\psi'' = n_0 l_0^{4l_0+1}\ {}^2l_0, (nl^N\alpha_1'' S_1'' L_1'', n_1 l_1) S'' L''; SL$.

5.5.2 The configuration interaction $nl^N \leftrightarrow nl^{N-2}n_1l_1^2$ or $nl^N \leftrightarrow nl^{N-2}n_1l_1n_2l_2$

The states ψ for nl^N configuration and ψ' for $nl^{N-2}n_1l_1^2$ or $nl^{N-2}n_1l_1n_2l_2$ configuration, respectively, are defined as follows:

$$\psi = n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha SL; SL,$$
$$\psi' = n_0 l_0^{4l_0+2}\ {}^1S, (nl^{N-2}\alpha_1' S_1' L_1', n_1 l_1^2\ \alpha_2' S_2' L_2') SL; SL \quad \text{or}$$
$$\psi' = n_0 l_0^{4l_0+2}\ {}^1S, (nl^{N-2}\alpha_1' S_1' L_1', (n_1 l_1 n_2 l_2) S_2' L_2') SL; SL.$$

The excitation of one electron from a closed $n_0 l_0^{4l_0+2}$ shell into an empty $n_1 l_1$ shell

$$-\sum_{\psi''} \langle \psi |\mathbf{G}| \psi'' \rangle \times \langle \psi'' |\mathbf{G}| \psi' \rangle = -\sum_{\psi''} \big[A(\psi,\psi'') + B(\psi,\psi'')\big] \times C(\psi'',\psi'), \tag{76}$$

where

$$\begin{aligned}
A(\psi,\psi'') &= \delta(S_1'',S)\ N\ (-1)^{2S+L+L''+L_1''+l+l_1+N+1}\ \frac{[S'',L'',L_1'']^{1/2}}{[S]^{1/2}} \begin{Bmatrix} t & l_0 & l_1 \\ L'' & L_1'' & L \end{Bmatrix} \\
&\times \sum_{\bar\alpha\bar S\bar L} (-1)^{2\bar S+\bar L} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \left(nl^N\alpha SL\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \begin{Bmatrix} L & t & L_1'' \\ l & \bar L & l \end{Bmatrix} \\
&\times (l_0\|\mathbf{C}^t\|l_1)(l\|\mathbf{C}^t\|l)R^t\,(n_0l_0nl,n_1l_1nl)\,, \qquad (77)\\
B(\psi,\psi'') &= N\ (-1)^{S+3S_1''+l+l_1+N+1}\ [S'',L'',S_1'',L_1'']^{1/2} \\
&\times \sum_{\bar\alpha\bar S\bar L} (-1)^{2\bar S} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \left(nl^N\alpha SL\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \begin{Bmatrix} \bar S & 1/2 & S \\ S'' & 1/2 & S_1'' \end{Bmatrix} \begin{Bmatrix} \bar L & l & L_1'' \\ l & t & l_1 \\ L & l_0 & L'' \end{Bmatrix} \\
&\times (l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0nl,nln_1l_1)\,, \qquad (78)
\end{aligned}$$

$C(\psi'',\psi')$ for $nl^{N-2}n_1l_1^2$ configuration

$$\begin{aligned}
C(\psi'',\psi') &= \sqrt{2N(N-1)}\ (-1)^{2S_1''+2S_1'+l+l_1+N}\ [S'',L'',S_1'',L_1'',S_2',L_2']^{1/2} \\
&\times \sum_{\hat\alpha'\hat S'\hat L'} (-1)^{\hat L'} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1',nl^2\hat\alpha'\hat S'\hat L'\right) [\hat S',\hat L']^{1/2} \\
&\times \begin{Bmatrix} S_1' & S_2' & S \\ \hat S' & 1/2 & 1/2 \\ S_1'' & 1/2 & S'' \end{Bmatrix} \begin{Bmatrix} L_1' & L_2' & L \\ \hat L' & l_1 & l_0 \\ L_1'' & l_1 & L'' \end{Bmatrix} \begin{Bmatrix} l & l_1 & t' \\ l_0 & l & \hat L' \end{Bmatrix} (l\|\mathbf{C}^{t'}\|l_1)(l\|\mathbf{C}^{t'}\|l_0)R^{t'}\,(nlnl,n_0l_0n_1l_1)\,, \qquad (79)
\end{aligned}$$

$C(\psi'',\psi')$ for $nl^{N-2}n_1l_1n_2l_2$ configuration

$$\begin{aligned}
C(\psi'',\psi') &= \sqrt{N(N-1)}\ (-1)^{S+L+S''+L''+S_1''+L_1''+S_1'+L_1'+l+l_0+l_2+N+1/2}\ [S'',L'',S_1'',L_1'',S_2',L_2']^{1/2} \\
&\times \sum_{\hat\alpha'\hat S'\hat L'} (-1)^{\hat L'} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1',nl^2\hat\alpha'\hat S'\hat L'\right) [\hat S',\hat L']^{1/2} \\
&\times \begin{Bmatrix} \hat S' & 1/2 & 1/2 \\ S_1' & S_2' & S \\ S_1'' & 1/2 & S'' \end{Bmatrix} \begin{Bmatrix} \hat L' & l_2 & l_0 \\ L_1' & L_2' & L \\ L_1'' & l_1 & L'' \end{Bmatrix} \begin{Bmatrix} l & l_0 & t' \\ l_2 & l & \hat L' \end{Bmatrix} (l\|\mathbf{C}^{t'}\|l_2)(l\|\mathbf{C}^{t'}\|l_0)R^{t'}\,(nlnl,n_0l_0n_2l_2)\,, \qquad (80)
\end{aligned}$$

and the perturbing virtual states are defined as $\psi'' = n_0l_0^{4l_0+1}\ {}^2l_0,(nl^N\alpha_1''S_1''L_1'',n_1l_1)S''L'';SL$.

5.5.3 The configuration interaction $nl^{N-1}n_1l_1 \leftrightarrow nl^{N-1}n_2l_2$

The states ψ for $nl^{N-1}n_1l_1$ configuration and ψ' for $nl^{N-1}n_2l_2$ configuration are defined as follows:

$$\begin{aligned}
\psi &= n_0l_0^{4l_0+2}\ {}^1S,(nl^{N-1}\alpha_1S_1L_1,n_1l_1)SL;SL,\\
\psi' &= n_0l_0^{4l_0+2}\ {}^1S,(nl^{N-1}\alpha_1'S_1'L_1',n_2l_2)SL;SL.
\end{aligned}$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^{N-1} shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle = -\sum_{\psi''}\big[A1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C(\psi'',\psi')+D(\psi'',\psi')\big], \qquad (81)$$

where

$$A1(\psi,\psi'') = \sqrt{N}\ (-1)^{3S+L+2S_1+L_1+2S''+3S_1''+l+l_0+l_1+N}\ [S'',L'',S_1'',L_1'']^{1/2} \begin{Bmatrix} 1/2 & S'' & S_1'' \\ 1/2 & S_1 & S \end{Bmatrix} \begin{Bmatrix} l_1 & L'' & L_1'' \\ l_0 & L_1 & L \end{Bmatrix}$$
$$\times \sum_{\bar\alpha\bar S\bar L} \delta(\bar S, S_1)\ \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \left\langle nl^{N-1}\bar\alpha\bar S\bar L\left\|\mathbf{U}^t\right\| nl^{N-1}\alpha_1S_1L_1\right\rangle \begin{Bmatrix} \bar L & t & L_1 \\ l_0 & L_1'' & l \end{Bmatrix}$$
$$\times (l\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_0)R^t\,(n_0l_0nl,nlnl)\,, \tag{82}$$

$$A2(\psi,\psi'') = \delta(S,S_1'')\ \sqrt{N}\ (-1)^{2S_1+2S''+L+L_1+L_1''+L''+l_0+l_1+N} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\alpha_1S_1L_1\right)$$
$$\times \frac{[S'',L'',L_1'']^{1/2}}{[S]^{1/2}} \begin{Bmatrix} t & l_1 & l \\ L_1 & L_1'' & L \end{Bmatrix} \begin{Bmatrix} L & t & L_1'' \\ l_1 & L'' & l_0 \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l)R^t\,(n_0l_0n_1l_1,n_1l_1nl)\,, \tag{83}$$

$$B2(\psi,\psi'') = \sqrt{N}\ (-1)^{2S_1+3S+2S''+3S_1''+N} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\alpha_1S_1L_1\right) [S'',L'',S_1'',L_1'']^{1/2}$$
$$\times \begin{Bmatrix} S_1 & 1/2 & S \\ S'' & 1/2 & S_1'' \end{Bmatrix} \begin{Bmatrix} L_1 & l & L_1'' \\ l_1 & t & l_1 \\ L & l_0 & L'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l)(l_1\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0n_1l_1,nln_1l_1)\,, \tag{84}$$

$$C1(\psi'',\psi') = \delta(S_1'',S)\ \sqrt{N}\ (-1)^{2S_1'+2S''+L+L_1'+L''+L_1''+l+l_1+N} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\alpha_1'S_1'L_1'\right)$$
$$\times \frac{[S'',L'',L_1'']^{1/2}}{[S]^{1/2}} \begin{Bmatrix} t' & l & l_2 \\ L_1' & L & L_1'' \end{Bmatrix} \begin{Bmatrix} L_1'' & t' & L \\ l_0 & L'' & l_1 \end{Bmatrix} (l\|\mathbf{C}^{t'}\|l_2)(l_1\|\mathbf{C}^{t'}\|l_0)R^{t'}\,(n_0l_0n_2l_2,n_1l_1nl)\,, \tag{85}$$

$$D1(\psi'',\psi') = \sqrt{N}\ (-1)^{2S_1'+3S_1''+3S+2S''+l_0+l+N} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\alpha_1'S_1'L_1'\right) [S'',L'',S_1'',L_1'']^{1/2}$$
$$\times \begin{Bmatrix} S_1' & 1/2 & S_1'' \\ S'' & 1/2 & S \end{Bmatrix} \begin{Bmatrix} L_1' & l_2 & L \\ l & t' & l_0 \\ L_1'' & l_1 & L'' \end{Bmatrix} (l\|\mathbf{C}^{t'}\|l_0)(l_1\|\mathbf{C}^{t'}\|l_2)R^{t'}\,(n_0l_0n_2l_2,nln_1l_1)\,, \tag{86}$$

and the perturbing virtual states are defined as $\psi'' = n_0l_0^{4l_0+1}\ {}^2l_0, (nl^N\alpha_1''S_1''L_1'', n_1l_1)S''L''; SL$.

The excitation of one electron from a closed $n_0l_0^{4l_0+2}$ shell to an empty n_2l_2 shell

$$-\sum_{\psi''} \langle\psi\,|\mathbf{G}|\,\psi''\rangle \times \langle\psi''\,|\mathbf{G}|\,\psi'\rangle =$$
$$-\sum_{\psi''}\Big(\big[A1(\psi,\psi'')+B1(\psi,\psi'')\big]\times\big[C1(\psi'',\psi')+D1(\psi'',\psi')\big]$$
$$+\big[A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C2(\psi'',\psi')+D2(\psi'',\psi')\big]\Big), \tag{87}$$

where

$$A1(\psi,\psi'') = \delta(S_1,S_1'')\ (-1)^{S''+S_1''+L+L''+L_2''+l_1+N+1}\ [S'',L'',S_2'',L_2'']^{1/2} \left\langle nl^{N-1}\alpha_1S_1L_1\left\|\mathbf{U}^t\right\| nl^{N-1}\alpha_1''S_1''L_1''\right\rangle$$
$$\times \begin{Bmatrix} 1/2 & S_1 & S \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_1 & l_2 & L_2'' \\ L_1 & t & L_1'' \\ L & l_0 & L'' \end{Bmatrix} (l\|\mathbf{C}^t\|l)(l_0\|\mathbf{C}^t\|l_2)R^t\,(n_0l_0nl,n_2l_2nl)\,, \tag{88}$$

$$B1(\psi,\psi'') = (N-1)\ [S'',L'',S_1,L_1,S_1'',L_1'',S_2'',L_2'']^{1/2} \sum_{\bar\alpha\bar S\bar L}(-1)^{S_1''+3\bar S+\bar L+L+L_1''+L_2''+L''+l_0+l_1+N+3/2}$$
$$\times \left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\bar\alpha\bar S\bar L\right) \left(nl^{N-1}\alpha_1S_1L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right) \begin{Bmatrix} \bar S & S_1 & 1/2 \\ 1/2 & S_2'' & S \end{Bmatrix} \begin{Bmatrix} S & \bar S & S_2'' \\ S_1'' & S'' & 1/2 \end{Bmatrix}$$
$$\times \begin{Bmatrix} l_1 & L & L_1 & \bar L \\ L_2'' & L'' & L_1'' & t \\ l_2 & l_0 & l & l \end{Bmatrix} (l\|\mathbf{C}^t\|l_2)(l_0\|\mathbf{C}^t\|l)R^t\,(n_0l_0nl,nln_2l_2)\,, \tag{89}$$

$$C1(\psi'',\psi') = \delta(S_1',S_1'')\ (-1)^{S_1'+S_2''+S''+L+L_1'+L_1''+L''+l_0+N+1}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} 1/2 & 1/2 & S_2'' \\ S'' & S_1' & S \end{Bmatrix} \times \begin{Bmatrix} l_2 & L_1' & L \\ l_1 & t' & l_0 \\ L_2'' & L_1'' & L'' \end{Bmatrix} \left\langle nl^{N-1}\alpha_1''S_1''L_1'' \left\| \mathbf{U}^{t'} \right\| nl^{N-1}\alpha_1'S_1'L_1' \right\rangle (l\|\mathbf{C}^{t'}\|l)(l_1\|\mathbf{C}^{t'}\|l_0)R^{t'}\,(n_0l_0nl,n_1l_1nl)\,, \tag{90}$$

$$D1(\psi'',\psi') = (N-1)\ [S_1',L_1',S'',L'',S_1'',L_1'',S_2'',L_2'']^{1/2} \sum_{\bar\alpha'\bar S'\bar L'} (-1)^{S_2''+S_1''+L_1''+3\bar S'+\bar L'+L+L''+N+3/2} \times \left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\bar\alpha'\bar S'\bar L'\right) \left(nl^{N-1}\alpha_1'S_1'L_1'\{|nl^{N-2}\bar\alpha'\bar S'\bar L'\right) \times \begin{Bmatrix} \bar S' & 1/2 & S_1' \\ 1/2 & S & S_2'' \end{Bmatrix} \begin{Bmatrix} S_2'' & \bar S' & S \\ 1/2 & S'' & S_1'' \end{Bmatrix} \begin{Bmatrix} L'' & L_2'' & L_1'' & \bar L' \\ L & l_2 & L_1' & t' \\ l_0 & l_1 & l & l \end{Bmatrix} (l\|\mathbf{C}^{t'}\|l_0)(l_1\|\mathbf{C}^{t'}\|l)R^{t'}\,(n_0l_0nl,nln_1l_1)\,, \tag{91}$$

$$A2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ (-1)^{2S+S_1+L_1+3S''+L''+2S_2''+L_2''+N}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S_2'' & S_1 & S'' \\ S & 1/2 & 1/2 \end{Bmatrix} \times \begin{Bmatrix} L_2'' & L_1 & L'' \\ L & l_0 & l_1 \end{Bmatrix} \begin{Bmatrix} l_0 & l_2 & t \\ l_1 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_2)(l_1\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0n_1l_1,n_2l_2n_1l_1)\,, \tag{92}$$

$$B2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ (-1)^{2S+S_1+L_1+3S''+L''+S_2''+N}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S_2'' & S_1 & S'' \\ S & 1/2 & 1/2 \end{Bmatrix} \times \begin{Bmatrix} L_2'' & L_1 & L'' \\ L & l_0 & l_1 \end{Bmatrix} \begin{Bmatrix} l_0 & l_1 & t \\ l_2 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l_2)R^t\,(n_0l_0n_1l_1,n_1l_1n_2l_2)\,, \tag{93}$$

$$C2(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ (-1)^{2S+S_1'+L_1'+3S''+L''+S_2''+l_1+l_2+N}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S_2'' & S_1' & S'' \\ S & 1/2 & 1/2 \end{Bmatrix} \times \begin{Bmatrix} L_2'' & L_1' & L'' \\ L & l_0 & l_2 \end{Bmatrix} \begin{Bmatrix} l_0 & l_1 & t' \\ l_2 & l_2 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l_1)(l_2\|\mathbf{C}^{t'}\|l_2)R^{t'}\,(n_0l_0n_2l_2,n_1l_1n_2l_2)\,, \tag{94}$$

$$D2(\psi'',\psi') = \delta(\alpha_1'S_1'L_1',\alpha_1''S_1''L_1'')\ (-1)^{2S+S_1'+L_1'+3S''+L''+2S_2''+L_2''+l_1+l_2+N}\ [S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S_2'' & S_1' & S'' \\ S & 1/2 & 1/2 \end{Bmatrix} \times \begin{Bmatrix} L_2'' & L_1' & L'' \\ L & l_0 & l_2 \end{Bmatrix} \begin{Bmatrix} l_0 & l_2 & t' \\ l_1 & l_2 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l_2)(l_2\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(n_0l_0n_2l_2,n_2l_2n_1l_1)\,, \tag{95}$$

and the perturbing virtual states are defined as $\psi'' = n_0l_0^{4l_0+1}\ {}^2l_0,(nl^{N-1}\alpha_1''S_1''L_1'',(n_1l_1n_2l_2)S_2''L_2'')S''L'';SL$.

5.5.4 The configuration interaction $nl^{N-1}n_1l_1 \leftrightarrow nl^{N-2}n_1l_1^2$

The states ψ for $nl^{N-1}n_1l_1$ configuration and ψ' for $nl^{N-2}n_1l_1^2$ configuration are defined as follows:

$$\psi = n_0l_0^{4l_0+2}\ {}^1S,(nl^{N-1}\alpha_1S_1L_1,n_1l_1)SL;SL,$$
$$\psi' = n_0l_0^{4l_0+2}\ {}^1S,(nl^{N-2}\alpha_1'S_1'L_1',n_1l_1^2\alpha_2'S_2'L_2')SL;SL.$$

The excitation of one electron from a closed $n_0l_0^{4l_0+2}$ shell to an open nl^{N-1} shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle = -\sum_{\psi''}A(\psi,\psi'')\times C(\psi'',\psi'), \tag{96}$$

where

$$A(\psi,\psi'') = \delta(S_1,\bar S)\ \sqrt{N}\ (-1)^{S+L+L_1+S_1''+l+l_0+l_1+N+1}\ [S'',L'',S_1'',L_1'']^{1/2} \begin{Bmatrix} 1/2 & S & S_1 \\ 1/2 & S_1'' & S'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1 \\ l_0 & L_1'' & L'' \end{Bmatrix} \times \sum_{\bar\alpha\bar S\bar L} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \left\langle nl^{N-1}\bar\alpha\bar S\bar L \left\| \mathbf{U}^{t'} \right\| nl^{N-1}\alpha_1S_1L_1 \right\rangle \begin{Bmatrix} \bar L & t & L_1 \\ l_0 & L_1'' & l \end{Bmatrix} \times (l\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_0)R^t\,(n_0l_0nl,nlnl)\,, \tag{97}$$

$$C(\psi'',\psi') = \sqrt{2N(N-1)}\,(-1)^{S+L+S_1''+L_1''+S_1'+L_1'+S''+L''+l+l_0+l_1+N+1/2}\,[S'',L'',S_1'',L_1'',S_2',L_2']^{1/2}$$
$$\times \sum_{\hat\alpha'\hat S'\hat L'} (-1)^{\hat L'}\,[\hat S',\hat L']^{1/2} \left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1',nl^2\hat\alpha'\hat S'\hat L'\right)$$
$$\times \begin{Bmatrix} \hat S' & 1/2 & 1/2 \\ S_1' & S_2' & S \\ S_1'' & 1/2 & S'' \end{Bmatrix} \begin{Bmatrix} \hat L' & l_1 & l_0 \\ L_1' & L_2' & L \\ L_1'' & l_1 & L'' \end{Bmatrix} \begin{Bmatrix} l & l_1 & t' \\ l_0 & l & \hat L' \end{Bmatrix} (l\|\mathbf{C}^{t'}\|l_1)(l\|\mathbf{C}^{t'}\|l_0)R^{t'}(nlnl,n_0l_0n_1l_1)\,, \tag{98}$$

and the perturbing virtual states are defined as $\psi'' = n_0l_0^{4l_0+1}\ ^2l_0,(nl^N\alpha_1''S_1''L_1'',n_1l_1)S''L'';SL$.

5.5.5 The configuration interaction $nl^{N-1}n_1l_1 \leftrightarrow nl^{N-2}n_2l_2^2$

The states ψ for $nl^{N-1}n_1l_1$ configuration and ψ' for $nl^{N-2}n_2l_2^2$ configuration are defined as follows:

$$\psi = n_0l_0^{4l_0+2}\ ^1S,(nl^{N-1}\alpha_1S_1L_1,n_1l_1)SL;SL,$$
$$\psi' = (n_0l_0^{4l_0+2}\ ^1S,nl^{N-2}\alpha_1'S_1'L_1')\alpha_1'S_1'L_1',n_2l_2^2\alpha_2'S_2'L_2';SL.$$

The excitation of one electron from a closed $n_0l_0^{4l_0+2}$ shell to an empty n_2l_2 shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle \times \langle\psi''\,|\mathbf{G}|\,\psi'\rangle =$$
$$-\sum_{\psi''}\Big(\big[A1(\psi,\psi'')+B1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C1(\psi,\psi'')+D1(\psi,\psi'')\big]\Big), \tag{99}$$

where

$$A1(\psi,\psi'') = (N-1)\,(-1)^{S+L+S''+L''+S_2''+L_2''+L_1+L_1''+l+l_2+N+1}\,\frac{[S_1,L_1,S_1'',L_1'',S_2'',L_2'',L'']^{1/2}}{[S'']^{1/2}}$$
$$\times \begin{Bmatrix} 1/2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1 \\ L'' & l_2 & L_2'' \end{Bmatrix} \sum_{\bar\alpha\bar S\bar L} \delta(S'',\bar S)\left(nl^{N-1}\alpha_1S_1L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\bar\alpha\bar S\bar L\right)$$
$$\times \begin{Bmatrix} \bar L & l & L_1 \\ l_2 & L'' & t \end{Bmatrix} \begin{Bmatrix} l & t & l_0 \\ L'' & L_1'' & \bar L \end{Bmatrix} (l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_2)R^t(n_0l_0nl,nln_2l_2)\,, \tag{100}$$

$$B1(\psi,\psi'') = \delta(S_1'',S_1)\,(N-1)\,(-1)^{S+L+2S_1+S_2''+L_2''+3S''+l_0+l+N+1}\,[S'',L'',S_2'',L_2'',L_1,L_1'']^{1/2} \begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1 & l_2 & t \end{Bmatrix}$$
$$\times \begin{Bmatrix} 1/2 & S & S_1 \\ S'' & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_1 & L & L_1 \\ L'' & l_2 & L_2'' \end{Bmatrix} \sum_{\bar\alpha\bar S\bar L}(-1)^{\bar L}\left(nl^{N-1}\alpha_1S_1L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\bar\alpha\bar S\bar L\right)$$
$$\times \begin{Bmatrix} t & l & l \\ \bar L & L_1 & L_1'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_2)(l\|\mathbf{C}^t\|l)R^t(n_0l_0nl,n_2l_2nl)\,, \tag{101}$$

$$A2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\,(-1)^{S+L+S''+L''+L_2''+l_0+l_1+N}\,[S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1 \\ 1/2 & S & S_2'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L'' & l_0 & L_1 \\ l_1 & L & L_2'' \end{Bmatrix} \begin{Bmatrix} l_0 & l_1 & t \\ l_2 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l_2)R^t(n_0l_0n_1l_1,n_1l_1n_2l_2)\,, \tag{102}$$

$$B2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\,(-1)^{S+L+S''+L''+S_2''+l_0+l_1+N}\,[S'',L'',S_2'',L_2'']^{1/2} \begin{Bmatrix} S'' & 1/2 & S_1 \\ 1/2 & S & S_2'' \end{Bmatrix}$$
$$\times \begin{Bmatrix} L'' & l_0 & L_1 \\ l_1 & L & L_2'' \end{Bmatrix} \begin{Bmatrix} l_0 & l_2 & t \\ l_1 & l_1 & L_2'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_2)(l_1\|\mathbf{C}^t\|l_1)R^t(n_0l_0n_1l_1,n_2l_2n_1l_1)\,, \tag{103}$$

$$C1(\psi'',\psi') = \delta(S_1',S'')\,\delta(S_2',S_2'')\,\sqrt{2(N-1)}\,(-1)^{2S+L+2S_1''+L_1''+L_2'+L_2''+l+N+1}$$
$$\times \left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1'\right)\frac{[S_1'',L_1'',L_2',L_2'',L'']^{1/2}}{[S']^{1/2}} \begin{Bmatrix} L'' & t' & L_1' \\ L_2' & L & L_2'' \end{Bmatrix} \begin{Bmatrix} L_2'' & L_2' & t' \\ l_2 & l_1 & l_2 \end{Bmatrix} \begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1' & t' & l \end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^{t'}\|l)(l_2\|\mathbf{C}^{t'}\|l_1)R^{t'}(n_0l_0n_2l_2,nln_1l_1)\,, \tag{104}$$

$$
\begin{aligned}
D1(\psi'',\psi') &= \sqrt{2(N-1)}\,(-1)^{2S+S'_1+2S''_1+3S''+L'_2+L''_2+l_0+l_2+N}\left(nl^{N-1}\alpha''_1S''_1L''_1\{|nl^{N-2}\alpha'_1S'_1L'_1\right)\\
&\times[S'_2,L'_2,S''_1,L''_1,S''_2,L''_2,S'',L'']^{1/2}\begin{Bmatrix}S & S''_1 & 1/2\\ 1/2 & S'_2 & S'_1\end{Bmatrix}\begin{Bmatrix}S & S''_1 & 1/2\\ 1/2 & S''_2 & S''\end{Bmatrix}\begin{bmatrix}l_2 & L & t' & L''_1\\ l_2 & l_1 & L'_1 & L''\\ L'_2 & l & L''_2 & l_0\end{bmatrix}\\
&\times(l_0\|\mathbf{C}^{t'}\|l_1)(l_2\|\mathbf{C}^{t'}\|l)R^{t'}\,(n_0l_0n_2l_2,n_1l_1nl)\,, \qquad (105)
\end{aligned}
$$

and the perturbing virtual states are defined as $\psi''=(n_0l_0^{4l_0+1}\ {}^2l_0,nl^{N-1}\alpha''_1S''_1L''_1)S''L'',(n_1l_1n_2l_2)S''_2L''_2;SL$.

5.5.6 The configuration interaction $nl^{N-1}n_1l_1\leftrightarrow nl^{N-2}n_2l_2n_1l_1$

The states ψ for $nl^{N-1}n_1l_1$ configuration and ψ' for $nl^{N-2}n_2l_2n_1l_1$ configuration are defined as follows:

$$
\begin{aligned}
\psi &= n_0l_0^{4l_0+2}\ {}^1S,(nl^{N-1}\alpha_1S_1L_1,n_1l_1)SL;SL,\\
\psi' &= (n_0l_0^{4l_0+2}\ {}^1S,nl^{N-2}\alpha'_1S'_1L'_1)\alpha'_1S'_1L'_1,(n_2l_2n_1l_1)S'_2L'_2;SL.
\end{aligned}
$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^{N-1} shell

$$
-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle=-\sum_{\psi''}\left[A1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi'')\right]\times C(\psi'',\psi'), \qquad (106)
$$

where

$$
\begin{aligned}
A1(\psi,\psi'') &= (N-1)\sqrt{N}\,[S_1,L_1,S'',L'',S''_1,L''_1]^{1/2}\begin{Bmatrix}1/2 & S_1 & S''_1\\ 1/2 & S'' & S\end{Bmatrix}\begin{Bmatrix}l_0 & L_1 & L''_1\\ l_1 & L'' & L\end{Bmatrix}\\
&\times\sum_{\bar\alpha\bar S\bar L,\hat\alpha\hat S\hat L}(-1)^{3S+L+\bar S+\bar L+\hat L+l+l_1+N+1}\left(nl^{N-1}\alpha_1S_1L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha''_1S''_1L''_1\{|nl^{N-2}\bar\alpha\bar S\bar L,nl^2\hat\alpha\hat S\hat L\right)\\
&\times[\hat S,\hat L]^{1/2}\begin{Bmatrix}S''_1 & \bar S & \hat S\\ 1/2 & 1/2 & S_1\end{Bmatrix}\begin{Bmatrix}L''_1 & \bar L & \hat L\\ l & l_0 & L_1\end{Bmatrix}\begin{Bmatrix}l & l_0 & t\\ l & l & \hat L\end{Bmatrix}(l\|\mathbf{C}^t\|l_0)(l\|\mathbf{C}^t\|l)R^t\,(n_0l_0nl,nlnl)\,, \qquad (107)\\
A2(\psi,\psi'') &= \sqrt{N}\,(-1)^{2S_1+S+3S''_1+N+1}\left(nl^N\alpha''_1S''_1L''_1\{|nl^{N-1}\alpha_1S_1L_1\right)[S'',L'',S''_1,L''_1]^{1/2}\\
&\times\begin{Bmatrix}S_1 & 1/2 & S''_1\\ S'' & 1/2 & S\end{Bmatrix}\begin{Bmatrix}L_1 & l_1 & L\\ l & t & l_0\\ L''_1 & l_1 & L''\end{Bmatrix}(l_0\|\mathbf{C}^t\|l)(l_1\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0n_1l_1,nln_1l_1)\,, \qquad (108)\\
B2(\psi,\psi'') &= \delta(S,S''_1)\,\sqrt{N}\,(-1)^{2S_1+2S+L+L_1+L''_1+L''+l_0+l_1+N+1}\left(nl^N\alpha''_1S''_1L''_1\{|nl^{N-1}\alpha_1S_1L_1\right)\\
&\times\frac{[S'',L'',L''_1]^{1/2}}{[S]^{1/2}}\begin{Bmatrix}t & l & l_1\\ L_1 & L & L''_1\end{Bmatrix}\begin{Bmatrix}L & t & L''_1\\ l_1 & L'' & l_0\end{Bmatrix}(l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l)R^t\,(n_0l_0n_1l_1,n_1l_1nl)\,, \qquad (109)\\
C(\psi'',\psi') &= \sqrt{N(N-1)}\,(-1)^{S'_1+S'_2+S''_1+S+S''+L+L''+L''_1+L'_1+L'_2+l_0+l+l_1+N+1/2}\,[S'',L'',S''_1,L''_1,S'_2L'_2]^{1/2}\\
&\times\sum_{\hat\alpha'\hat S'\hat L'}(-1)^{\hat L'}\,[\hat S',\hat L']^{1/2}\left(nl^N\alpha''_1S''_1L''_1\{|nl^{N-2}\alpha'_1S'_1L'_1,nl^2\hat\alpha'\hat S'\hat L'\right)\\
&\times\begin{Bmatrix}\hat S' & 1/2 & 1/2\\ S'_1 & S'_2 & S\\ S''_1 & 1/2 & S''\end{Bmatrix}\begin{Bmatrix}\hat L' & l_2 & l_0\\ L'_1 & L'_2 & L\\ L''_1 & l_1 & L''\end{Bmatrix}\begin{Bmatrix}l & l_0 & t'\\ l_2 & l & \hat L'\end{Bmatrix}(l\|\mathbf{C}^{t'}\|l_0)(l\|\mathbf{C}^{t'}\|l_2)R^{t'}\,(nlnl,n_0l_0n_2l_2)\,, \qquad (110)
\end{aligned}
$$

and the perturbing virtual states are defined as $\psi''=n_0l_0^{4l_0+1}\ {}^2l_0,(nl^N\alpha''_1S''_1L''_1,n_1l_1)S''L'';SL$.

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open n_1l_1 shell

$$
-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle=-\sum_{\psi''}\left[A1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi'')\right]\times\left[C1(\psi,\psi'')+D1(\psi,\psi'')\right], \qquad (111)
$$

where

$$A1(\psi,\psi'') = \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \sqrt{2}\ (-1)^{2S+3S''+S_1''+L_1''+L''+L_2''+l_0+l_1+N}\ [S'', L'', S_2'', L_2'']^{1/2}$$
$$\times \begin{Bmatrix} 1/2 & S & S'' \\ S_1 & S_2'' & 1/2 \end{Bmatrix} \begin{Bmatrix} l_0 & L & L'' \\ L_1 & L_2'' & l_1 \end{Bmatrix} \begin{Bmatrix} l_1 & l_0 & t \\ l_1 & l_1 & L_2'' \end{Bmatrix} (l_1\|\mathbf{C}^t\|l_0)(l_1\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0n_1l_1, n_1l_1n_1l_1)\,, \tag{112}$$

$$A2(\psi,\psi'') = (N-1)\sqrt{2}\ [S_1, L_1, S'', L'', S_1'', L_1'', S_2'', L_2'']^{1/2} \sum_{\bar\alpha\bar S\bar L} (-1)^{S_1''+L_1''+3\bar S+\bar L+L+L''+L_2''+N+3/2}$$
$$\times \left(nl^{N-1}\alpha_1 S_1 L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\left(nl^{N-1}\alpha_1'' S_1'' L_1''\{|nl^{N-2}\bar\alpha\bar S\bar L\right)$$
$$\times \begin{Bmatrix} S & \bar S & S_2'' \\ S_1'' & S'' & 1/2 \end{Bmatrix} \begin{Bmatrix} S & \bar S & S_2'' \\ 1/2 & 1/2 & S_1 \end{Bmatrix} \begin{Bmatrix} l & t & l_0 & L \\ \bar L & l & L_1 & L_2'' \\ L_1'' & l_1 & L'' & l_1 \end{Bmatrix} (l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0nl, nln_1l_1)\,, \tag{113}$$

$$B2(\psi,\psi'') = \delta(S_1, S_1'')\ (N-1)\sqrt{2}\ [L_1, L_1'', S'', L'', S_2'', L_2'']^{1/2} \sum_{\bar\alpha\bar S\bar L} (-1)^{S_1+L_1+2\bar S+\bar L+3S''+L''+L+L_2''+l+l_0+N}$$
$$\times \left(nl^{N-1}\alpha_1 S_1 L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\left(nl^{N-1}\alpha_1'' S_1'' L_1''\{|nl^{N-2}\bar\alpha\bar S\bar L\right)$$
$$\times \begin{Bmatrix} S_1 & S'' & S_2'' \\ 1/2 & 1/2 & S \end{Bmatrix} \begin{Bmatrix} L_1'' & L_1 & t \\ l & l & \bar L \end{Bmatrix} \begin{Bmatrix} L_1'' & L_1 & t \\ L'' & L & l_0 \\ L_2'' & l_1 & l_1 \end{Bmatrix} (l_0\|\mathbf{C}^t\|l_1)(l\|\mathbf{C}^t\|l)R^t\,(n_0l_0nl, n_1l_1nl)\,, \tag{114}$$

$$C1(\psi'',\psi') = \delta(S_2', S_2'')\ \sqrt{2(N-1)}\ (-1)^{S+S_1''+L_2''+L_2'+N+1/2}\left(nl^{N-1}\alpha_1'' S_1'' L_1''\{|nl^{N-2}\alpha_1' S_1' L_1'\right)$$
$$\times [S'', L'', S_1'', L_1'', L_2', L_2'']^{1/2} \begin{Bmatrix} S_2' & S_1' & S \\ 1/2 & S'' & S_1'' \end{Bmatrix} \begin{Bmatrix} L_2' & L_2'' & t' \\ l_1 & l_2 & l_1 \end{Bmatrix} \begin{Bmatrix} L_2' & L_2'' & t' \\ L_1' & L_1'' & l \\ L & L'' & l_0 \end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^{t'}\|l)(l_2\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(n_0l_0n_2l_2, nln_1l_1)\,, \tag{115}$$

$$D1(\psi'',\psi') = \sqrt{2(N-1)}\ (-1)^{S+S''+S_1''+S_1'+l_0+l_1+N}\left(nl^{N-1}\alpha_1'' S_1'' L_1''\{|nl^{N-2}\alpha_1' S_1' L_1'\right)$$
$$\times [S'', L'', S_1'', L_1'', S_2', L_2', S_2'', L_2'']^{1/2} \begin{Bmatrix} S_1'' & 1/2 & S \\ S_2' & S_1' & 1/2 \end{Bmatrix} \begin{Bmatrix} S_1'' & 1/2 & S \\ 1/2 & S'' & S_2'' \end{Bmatrix} \begin{Bmatrix} l_2 & t' & l & L_1'' \\ l_1 & l_1 & L_2'' & L \\ L_2' & l_0 & L_1' & L'' \end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^{t'}\|l_1)(l_2\|\mathbf{C}^{t'}\|l)R^{t'}\,(n_0l_0n_2l_2, n_1l_1nl)\,, \tag{116}$$

and the perturbing virtual states are defined as $\psi'' = n_0l_0^{4l_0+1}\ {}^2l_0, (nl^{N-1}\alpha_1'' S_1'' L_1'', n_1l_1^2\alpha_2'' S_2'' L_2'')S''L''; SL$.

5.5.7 The configuration interaction $nl^{N-1}n_1l_1 \leftrightarrow nl^{N-2}n_1l_1n_2l_2$

The states ψ for $nl^{N-1}n_1l_1$ configuration and ψ' for $nl^{N-2}n_1l_1n_2l_2$ configuration are defined as follows:

$$\psi = n_0l_0^{4l_0+2}\ {}^1S, (nl^{N-1}\alpha_1 S_1 L_1, n_1l_1)SL; SL,$$
$$\psi' = (n_0l_0^{4l_0+2}\ {}^1S, nl^{N-2}\alpha_1' S_1' L_1')\alpha_1' S_1' L_1', (n_1l_1n_2l_2)S_2' L_2'; SL$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^{N-1} shell

Through the proper recoupling procedures fourth term $C(\psi'',\psi')$ of the sum in eq. (106) must be multiplied by a phase factor equal to $(-1)^{l_1+l_2+3S_2'+L_2'}$, and the perturbing virtual states are defined as

$$\psi'' = n_0l_0^{4l_0+1}\ {}^2l_0, (nl^N\alpha_1'' S_1'' L_1'', n_1l_1)S''L''; SL.$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open n_1l_1 shell

Through the proper recoupling procedures, the fourth and fifth $(C1(\psi,\psi'')+D1(\psi,\psi''))$ term of the sum in eq. (111) must be multiplied by a phase factor equal to $(-1)^{l_1+l_2+3S_2'+L_2'}$, and the perturbing virtual states are defined as

$$\psi'' = n_0l_0^{4l_0+1}\ {}^2l_0, (nl^{N-1}\alpha_1'' S_1'' L_1'', n_1l_1^2\alpha_2'' S_2'' L_2'')S''L''; SL.$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an empty n_2l_2 shell

$$
\begin{aligned}
&-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle=\\
&-\sum_{\psi''}\big[A(\psi,\psi'')+B(\psi,\psi'')\big]\times\big[C1(\psi,\psi'')+D1(\psi,\psi'')+C2(\psi,\psi'')+D2(\psi,\psi'')\big],
\end{aligned}
\tag{117}
$$

where

$$
\begin{aligned}
A(\psi,\psi'')&=\delta(S_1,S_1'')\,(-1)^{S+2S_1''+S_2''+3S''+L_2''+L+L_1+l_0+N+1}\,[S'',L'',S_2'',L_2'']^{1/2}\,\left\langle nl^{N-1}\alpha_1S_1L_1\left\|\mathbf{U}^t\right\|nl^{N-1}\alpha_1''S_1''L_1''\right\rangle\\
&\times\begin{Bmatrix}1/2 & S_1'' & S''\\ S & S_2'' & 1/2\end{Bmatrix}\begin{Bmatrix}l_2 & l_1 & L_2''\\ L & L'' & L_1\end{Bmatrix}\begin{Bmatrix}t & L_1 & L_1''\\ L'' & l_0 & l_2\end{Bmatrix}(l\|\mathbf{C}^t\|l)(l_0\|\mathbf{C}^t\|l_2)R^t\left(n_0l_0nl,n_2l_2nl\right), \qquad (118)\\
B(\psi,\psi'')&=(N-1)\,\frac{[S_1,L_1,L'',S_1'',L_1'',S_2'',L_2'']^{1/2}}{[S'']^{1/2}}\begin{Bmatrix}L_2'' & l_2 & l_1\\ L_1 & L & L''\end{Bmatrix}\\
&\times\sum_{\bar\alpha\bar S\bar L}\delta(\bar S,S'')\,(-1)^{S+L+2S_1''+L_1''+S_2''+L_2''+L_1+L''+3\bar S+l+l_0+N}\\
&\times\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\left(nl^{N-1}\alpha_1S_1L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\\
&\times\begin{Bmatrix}S & \bar S & S_2''\\ 1/2 & 1/2 & S_1\end{Bmatrix}\begin{Bmatrix}l_2 & t & l\\ \bar L & L_1 & L''\end{Bmatrix}\begin{Bmatrix}t & l_0 & l\\ L_1'' & \bar L & L''\end{Bmatrix}(l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_2)R^t\left(n_0l_0nl,nln_2l_2\right), \qquad (119)\\
C1(\psi'',\psi')&=\delta(S_2',S_2'')\,\delta(S_1',S'')\,\sqrt{N-1}\,(-1)^{L+L_1''+l_0+l_1+l_2+N}\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1'\right)\\
&\times\frac{[S_1'',L_1'',L_2'',L_2',L'']^{1/2}}{[S_1']^{1/2}}\begin{Bmatrix}L_2' & L_2'' & t'\\ l_2 & l_2 & l_1\end{Bmatrix}\begin{Bmatrix}L_1' & t' & L''\\ L_2'' & L & L_2'\end{Bmatrix}\begin{Bmatrix}l_0 & l & t'\\ L_1' & L'' & L_1''\end{Bmatrix}\\
&\times(l_0\|\mathbf{C}^{t'}\|l)(l_2\|\mathbf{C}^{t'}\|l_2)R^{t'}\left(n_0l_0n_2l_2,nln_2l_2\right), \qquad (120)\\
D1(\psi'',\psi')&=\sqrt{N-1}\,(-1)^{S''+3S_2''+3S_1'+3S_2'+l_0+l_2+N+1}\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1'\right)\\
&\times[S'',L'',S_1'',L_1'',S_2',L_2',S_2'',L_2'']^{1/2}\begin{Bmatrix}S_1' & S & S_2'\\ 1/2 & 1/2 & S_1''\end{Bmatrix}\begin{Bmatrix}S_1'' & S'' & 1/2\\ S_2'' & 1/2 & S\end{Bmatrix}\begin{bmatrix}L_2'' & l_0 & L_2' & l\\ l_1 & L & t' & L_1''\\ l_2 & l_2 & L'' & L_1'\end{bmatrix}\\
&\times(l_0\|\mathbf{C}^{t'}\|l_2)(l_2\|\mathbf{C}^{t'}\|l)R^{t'}\left(n_0l_0n_2l_2,n_2l_2nl\right), \qquad (121)\\
C2(\psi'',\psi')&=\delta(S_2',S_2'')\,\delta(S_1',S'')\,\sqrt{N-1}\,(-1)^{2S+L+2S_2'+L_2'+2S_1''+L_1''+L_2''+l+l_1+l_2+N+1}\\
&\times\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1'\right)\frac{[S_1'',L_1'',L_2'',L_2',L'']^{1/2}}{[S_1']^{1/2}}\begin{Bmatrix}t' & l_1 & l_1\\ l_2 & L_2'' & L_2'\end{Bmatrix}\begin{Bmatrix}L_1' & t' & L''\\ L_2'' & L & L_2'\end{Bmatrix}\begin{Bmatrix}l & L_1' & L_1''\\ L'' & l_0 & t'\end{Bmatrix}\\
&\times(l_0\|\mathbf{C}^{t'}\|l)(l_1\|\mathbf{C}^{t'}\|l_1)R^{t'}\left(n_0l_0n_1l_1,nln_1l_1\right), \qquad (122)\\
D2(\psi'',\psi')&=\sqrt{N-1}\,(-1)^{2S''+S_2''+2S_1'+3S_2'+L_1'+L''+l+l_1+N+1}\,2(2l_1+1)\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1'\right)\\
&\times[S'',L'',S_1'',L_1'',S_2',L_2',S_2'',L_2'']^{1/2}\begin{bmatrix}S_2' & 1/2 & S_2'' & 1/2\\ 1/2 & S & 0 & S_1''\\ 1/2 & 1/2 & S_1' & S''\end{bmatrix}\begin{bmatrix}L_1' & L_2' & l_1 & l_1 & l\\ L & l_2 & 0 & t' & L_1''\\ L'' & L_2'' & l_1 & l_1 & l_0\end{bmatrix}\\
&\times(l_0\|\mathbf{C}^{t'}\|l_1)(l_1\|\mathbf{C}^{t'}\|l)R^{t'}\left(n_0l_0n_1l_1,n_1l_1nl\right), \qquad (123)
\end{aligned}
$$

and the perturbing virtual states are defined as $\psi''=(n_0l_0^{4l_0+1}\,{}^2l_0,nl^{N-1}\alpha_1''S_1''L_1'')S''L'',(n_1l_1n_2l_2)S_2''L_2'';SL$.

5.5.8 The configuration interaction $nl^{N-1}n_1l_1\leftrightarrow nl^{N-2}n_2l_2n_3l_3$

The states ψ for $nl^{N-1}n_1l_1$ configuration and ψ' for $nl^{N-2}n_2l_2n_3l_3$ configuration are defined as follows:

$$
\begin{aligned}
\psi&=n_0l_0^{4l_0+2}\,{}^1S,(nl^{N-1}\alpha_1S_1L_1,n_1l_1)SL;SL,\\
\psi'&=(n_0l_0^{4l_0+2}\,{}^1S,nl^{N-2}\alpha_1'S_1'L_1')\alpha_1'S_1'L_1',(n_2l_2n_3l_3)S_2'L_2';SL.
\end{aligned}
$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an empty n_2l_2 shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle=-\sum_{\psi''}\big[A(\psi,\psi'')+B(\psi,\psi'')\big]\times\big[C(\psi,\psi'')+D(\psi,\psi'')\big], \tag{124}$$

where

$$\begin{aligned}A(\psi,\psi'')=&\ \delta(S_1,S_1'')\ (-1)^{S+2S_1''+3S''+L+L_1+l_0+l_1+l_2+N+1}\ [S'',L'',S_2'',L_2'']^{1/2}\\&\times\left\langle nl^{N-1}\alpha_1S_1L_1\left\|\mathbf{U}^t\right\|nl^{N-1}\alpha_1''S_1''L_1''\right\rangle\begin{Bmatrix}1/2 & S_1'' & S''\\ S & S_2'' & 1/2\end{Bmatrix}\begin{Bmatrix}l_2 & l_1 & L_2''\\ L & L'' & L_1\end{Bmatrix}\begin{Bmatrix}t & L_1 & L_1''\\ L'' & l_0 & l_2\end{Bmatrix}\\&\times(l\|\mathbf{C}^t\|l)(l_0\|\mathbf{C}^t\|l_2)R^t\,(n_0l_0nl,n_2l_2nl)\,, \qquad (125)\\B(\psi,\psi'')=&\ (N-1)\ \frac{[S_1,L_1,L'',S_1'',L_1'',S_2'',L_2'']^{1/2}}{[S'']^{1/2}}\begin{Bmatrix}L_2'' & l_2 & l_1\\ L_1 & L & L''\end{Bmatrix}\\&\times\sum_{\bar\alpha\bar S\bar L}\delta(\bar S,S'')\ (-1)^{S+L+2S_1''+L_1''+L_1+L''+3\bar S+l+l_0+l_1+l_2+N}\\&\times\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\left(nl^{N-1}\alpha_1S_1L_1\{|nl^{N-2}\bar\alpha\bar S\bar L\right)\\&\times\begin{Bmatrix}S & \bar S & S_2''\\ 1/2 & 1/2 & S_1\end{Bmatrix}\begin{Bmatrix}l_2 & t & l\\ \bar L & L_1 & L''\end{Bmatrix}\begin{Bmatrix}t & l_0 & l\\ L_1'' & \bar L & L''\end{Bmatrix}(l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_2)R^t\,(n_0l_0nl,nln_2l_2)\,, \qquad (126)\\C(\psi'',\psi')=&\ \delta(S_2',S_2'')\ \delta(S_1',S'')\ \sqrt{N-1}\ (-1)^{L+L_2'+L_1''+l_0+l_1+N}\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1'\right)\\&\times\frac{[S_1'',L_1'',L_2'',L_2',L'']^{1/2}}{[S_1']^{1/2}}\ \begin{Bmatrix}L_2' & L_2'' & t'\\ l_1 & l_3 & l_2\end{Bmatrix}\begin{Bmatrix}L_1' & t' & L''\\ L_2'' & L & L_2'\end{Bmatrix}\begin{Bmatrix}l_0 & l & t'\\ L_1' & L'' & L_1''\end{Bmatrix}\\&\times(l_0\|\mathbf{C}^{t'}\|l)(l_3\|\mathbf{C}^{t'}\|l_2)R^{t'}\,(n_0l_0n_3l_3,nln_1l_1)\,, \qquad (127)\\D(\psi'',\psi')=&\ \sqrt{N-1}\ (-1)^{S''+3S_2''+3S_1'+3S_2'+l_0+l_3+N+1}\left(nl^{N-1}\alpha_1''S_1''L_1''\{|nl^{N-2}\alpha_1'S_1'L_1'\right)\\&\times[S'',L'',S_1'',L_1'',S_2',L_2',S_2'',L_2'']^{1/2}\begin{Bmatrix}S_1' & S & S_2'\\ 1/2 & 1/2 & S_1''\end{Bmatrix}\begin{Bmatrix}S_1'' & S'' & 1/2\\ S_2'' & 1/2 & S\end{Bmatrix}\begin{bmatrix}L_2'' & l_0 & L_2' & l\\ l_2 & L & t' & L_1''\\ l_1 & l_3 & L'' & L_1'\end{bmatrix}\\&\times(l_0\|\mathbf{C}^{t'}\|l_1)(l_3\|\mathbf{C}^{t'}\|l)R^{t'}\,(n_0l_0n_3l_3,n_1l_1nl)\,, \qquad (128)\end{aligned}$$

and the perturbing virtual states are defined as $\psi''=(n_0l_0^{4l_0+1}\ {}^2l_0,nl^{N-1}\alpha_1''S_1''L_1'')S''L'',(n_2l_2n_1l_1)S_2''L_2'';SL$.

5.5.9 The configuration interaction $nl^Nn_1l_1n_3l_3\leftrightarrow nl^Nn_2l_2n_3l_3$

The states ψ for $nl^Nn_1l_1n_3l_3$ configuration and ψ' for $nl^Nn_2l_2n_3l_3$ configuration are defined as follows:

$$\begin{aligned}\psi&=(n_0l_0^{4l_0+2}\ {}^1S,nl^N\alpha_1S_1L_1)\alpha_1S_1L_1,(n_1l_1n_3l_3)S_2L_2;SL,\\\psi'&=(n_0l_0^{4l_0+2}\ {}^1S,nl^N\alpha_1'S_1'L_1')\alpha_1'S_1'L_1',(n_2l_2n_3l_3)S_2'L_2';SL.\end{aligned}$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^N shell

$$\begin{aligned}&-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle=\\&-\sum_{\psi''}\big[A1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C1(\psi'',\psi')+D1(\psi'',\psi')\big],\end{aligned} \tag{129}$$

where

$$\begin{aligned}A1(\psi,\psi'')=&\ \delta(S_1L_1,S''L'')\ \delta(S_2L_2,S_2''L_2'')\ \sqrt{N+1}\ (-1)^{2S+2S_1''+L_1''+L_1+l+N+1}\ \frac{[S_1'',L_1'']^{1/2}}{[S_1,L_1]^{1/2}}\\&\times\sum_{\bar\alpha\bar S\bar L}\delta(\bar S,S_1)\ \left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\bar\alpha\bar S\bar L\right)\left\langle nl^N\bar\alpha\bar S\bar L\left\|\mathbf{U}^t\right\|nl^N\alpha_1S_1L_1\right\rangle\begin{Bmatrix}\bar L & t & L_1\\ l_0 & L_1'' & l\end{Bmatrix}\\&\times(l\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_0)R^t\,(n_0l_0nl,nlnl)\,, \qquad (130)\end{aligned}$$

$$A2(\psi,\psi'') = \sqrt{N+1}\,(-1)^{S_1+2S+3S''+2S_1''+L_2+L_2''+N+l_1+l+l_0}\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)$$
$$\times[S_2,L_2,S'',L'',S_1'',L_1'',S_2'',L_2'']^{1/2}\begin{Bmatrix}1/2 & S & S_1''\\ S_1 & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix}1/2 & S & S_1''\\ S'' & 1/2 & S_2''\end{Bmatrix}\begin{bmatrix}l_1 & l_1 & L_1 & L''\\ L_2 & l & L_2'' & l_0\\ l_3 & L & t & L_1''\end{bmatrix}$$
$$\times(l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l)R^t\left(n_0l_0n_1l_1,n_1l_1nl\right), \tag{131}$$
$$B2(\psi,\psi'') = \delta(S_1,S'')\,\delta(S_2,S_2'')\,\sqrt{N+1}\,(-1)^{2S+2S_1''+L+L_2+L_1''+L_2''+l_0+l_1+l_3+N+1}$$
$$\times\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)\frac{[S_1'',L_1'',L_2,L_2'',L'']^{1/2}}{[S_1]^{1/2}}\begin{Bmatrix}L_1 & l & L_1''\\ l_0 & L'' & t\end{Bmatrix}\begin{Bmatrix}L_2'' & L & L''\\ L_1 & t & L_2\end{Bmatrix}\begin{Bmatrix}L_2 & L_2'' & t\\ l_1 & l_1 & l_3\end{Bmatrix}$$
$$\times(l_0\|\mathbf{C}^t\|l)(l_1\|\mathbf{C}^t\|l_1)R^t\left(n_0l_0n_1l_1,nln_1l_1\right), \tag{132}$$
$$C1(\psi'',\psi') = \sqrt{N+1}\,(-1)^{S_1'+2S_1''+2S+3S''+L_2'+L_2''+l_0+l_2+N}\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right)$$
$$\times[S_2',L_2',S_2'',L_2'',S'',L'',S_1'',L_1'']^{1/2}\begin{Bmatrix}1/2 & S & S_1''\\ S'' & 1/2 & S_2''\end{Bmatrix}\begin{Bmatrix}1/2 & S & S_1''\\ S_1' & 1/2 & S_2'\end{Bmatrix}\begin{bmatrix}l_1 & l_2 & L'' & L_1'\\ L_2'' & l_0 & L_2' & l\\ l_3 & L & t' & L_1''\end{bmatrix}$$
$$\times(l\|\mathbf{C}^{t'}\|l_2)(l_1\|\mathbf{C}^{t'}\|l_0)R^{t'}\left(n_0l_0n_2l_2,n_1l_1nl\right), \tag{133}$$
$$D1(\psi'',\psi') = \delta(S_1',S'')\,\delta(S_2',S_2'')\,\sqrt{N+1}\,(-1)^{2S+2S_1''+L+L_2'+L_1''+L_2''+l+l_2+l_3+N+1}$$
$$\times\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1'S_1'L_1'\right)\frac{[S_1'',L_1'',L_2',L_2'',L'']^{1/2}}{[S_1']^{1/2}}\begin{Bmatrix}l & t' & l_0\\ L'' & L_1'' & L_1'\end{Bmatrix}\begin{Bmatrix}t' & l_1 & l_2\\ l_3 & L_2' & L_2''\end{Bmatrix}\begin{Bmatrix}L_2'' & t' & L_2'\\ L_1' & L & L''\end{Bmatrix}$$
$$\times(l\|\mathbf{C}^{t'}\|l_0)(l_1\|\mathbf{C}^{t'}\|l_2)R^{t'}\left(n_0l_0n_2l_2,nln_1l_1\right), \tag{134}$$

and the perturbing virtual states are defined as

$$\psi'' = (n_0l_0^{4l_0+1}\ {}^2l_0,nl^{N+1}\alpha_1''S_1''L_1'')S''L'',(n_1l_1n_3l_3)S_2''L_2'';SL.$$

5.5.10 The configuration interaction $nl^Nn_3l_3n_1l_1 \leftrightarrow nl^Nn_3l_3n_2l_2$

The states ψ for $nl^Nn_3l_3n_1l_1$ configuration and ψ' for $nl^Nn_3l_3n_2l_2$ configuration are defined as follows:

$$\psi = (n_0l_0^{4l_0+2}\ {}^1S,nl^N\alpha_1S_1L_1)\alpha_1S_1L_1,(n_3l_3n_1l_1)S_2L_2;SL,$$
$$\psi' = (n_0l_0^{4l_0+2}\ {}^1S,nl^N\alpha_1'S_1'L_1')\alpha_1'S_1'L_1',(n_3l_3n_2l_2)S_2'L_2';SL.$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open nl^N shell

Through the proper recoupling procedures, the first, second and third $(A1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi''))$ term of the sum in eq. (129) must be multiplied by a phase factor equal to $(-1)^{S_2+L_2+S_2''+L_2''}$ and the fourth and fifth $((C1(\psi,\psi'')+D1(\psi,\psi''))$ term of the sum in eq. (129) must be multiplied by a phase factor equal to $(-1)^{l_1+l_2+S_2'+L_2'+S_2''+L_2''}$, and the perturbing virtual states are defined as:

$$\psi'' = (n_0l_0^{4l_0+1}\ {}^2l_0,nl^{N+1}\alpha_1''S_1''L_1'')S''L'',(n_3l_3n_1l_1)S_2''L_2'';SL.$$

5.5.11 The configuration interaction $nl^Nn_1l_1n_2l_2 \leftrightarrow nl^{N-1}n_1l_1^2n_2l_2$

The states ψ for $nl^Nn_1l_1n_2l_2$ configuration and ψ' for $nl^{N-1}n_1l_1^2n_2l_2$ configuration are defined as follows:

$$\psi = (n_0l_0^{4l_0+2}\ {}^1S,nl^N\alpha_1S_1L_1)\alpha_1S_1L_1,(n_1l_1n_2l_2)S_2L_2)SL;SL,$$
$$\psi' = (n_0l_0^{4l_0+2}\ {}^1S,nl^{N-1}\alpha_1'S_1'L_1')\alpha_1'S_1'L_1',(n_1l_1^2\alpha_2'S_2'L_2',n_2l_2)S_3'L_3';SL.$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open nl shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle =$$
$$-\sum_{\psi''}\left[A1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi'')+A3(\psi,\psi'')+B3(\psi,\psi'')\right]\times C(\psi'',\psi'), \tag{135}$$

where

$$\begin{aligned}
A1(\psi,\psi'') &= \delta(S_1L_1,S''L'')\ \delta(S_2L_2,S_2''L_2'')\ N\sqrt{N+1}\sum_{\bar\alpha\bar S\bar L,\hat\alpha\hat S\hat L}(-1)^{2S_1+3S_1''+L_1''+\bar S+\bar L+\hat L+l+l_0+N}\\
&\times\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L,nl^2\hat\alpha\hat S\hat L\right)\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)[S_1'',L_1'',\hat S,\hat L]^{1/2}\\
&\times\begin{Bmatrix}\bar S & S_1 & 1/2\\ 1/2 & \hat S & S_1''\end{Bmatrix}\begin{Bmatrix}\bar L & L_1 & l\\ l_0 & \hat L & L_1''\end{Bmatrix}\begin{Bmatrix}l & l_0 & t\\ l & l & \hat L\end{Bmatrix}(l\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_0)R^t\,(n_0l_0nl,nlnl)\,, && (136)\\
A2(\psi,\psi'') &= \delta(S_1,S_1'')\ \delta(S_2,S_2'')\ \sqrt{N+1}\ (-1)^{2S+L+2S_1''+L_1''+l+l_1+l_2+N+1}\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)\\
&\times\frac{[S_1'',L_1'',L_2,L_2'',L'']^{1/2}}{[S_1]^{1/2}}\begin{Bmatrix}l_2 & L_2 & l_1\\ L_2'' & l_2 & t\end{Bmatrix}\begin{Bmatrix}L_2 & L_1 & L\\ L'' & L_2'' & t\end{Bmatrix}\begin{Bmatrix}L_1 & l & L_1''\\ l_0 & L'' & t\end{Bmatrix}\\
&\times(l_0\|\mathbf{C}^t\|l)(l_2\|\mathbf{C}^t\|l_2)R^t\,(n_0l_0n_2l_2,nln_2l_2)\,, && (137)\\
B2(\psi,\psi'') &= \sqrt{N+1}\ (-1)^{2S+3S_1+S_2+2S_1''+S_2''+S''+l_0+l_2+N}\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)\\
&\times[S_2,L_2,S_2'',L_2'',S'',L'',S_1'',L_1'']^{1/2}\begin{Bmatrix}1/2 & S & S_1''\\ S_1 & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix}1/2 & S & S_1''\\ S'' & 1/2 & S_2''\end{Bmatrix}\begin{bmatrix}L_2 & l & L_2'' & l_0\\ L & l_1 & L_1'' & t\\ L_1 & L'' & l_2 & l_2\end{bmatrix}\\
&\times(l_0\|\mathbf{C}^t\|l_2)(l_2\|\mathbf{C}^t\|l)R^t\,(n_0l_0n_2l_2,n_2l_2nl)\,, && (138)\\
A3(\psi,\psi'') &= \delta(S_1,S_1'')\ \delta(S_2,S_2'')\ \sqrt{N+1}\ (-1)^{S_2+L_2+S_2''+L_2''+2S+L+2S_1''+L_1''+l+l_1+l_2+N+1}\\
&\times\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)\frac{[S_1'',L_1'',L_2,L_2'',L'']^{1/2}}{[S_1]^{1/2}}\begin{Bmatrix}l_1 & L_2 & l_2\\ L_2'' & l_1 & t\end{Bmatrix}\begin{Bmatrix}L_2 & L_1 & L\\ L'' & L_2'' & t\end{Bmatrix}\begin{Bmatrix}L_1 & l & L_1''\\ l_0 & L'' & t\end{Bmatrix}\\
&\times(l_0\|\mathbf{C}^t\|l)(l_1\|\mathbf{C}^t\|l_1)R^t\,(n_0l_0n_1l_1,nln_1l_1)\,, && (139)\\
B3(\psi,\psi'') &= \sqrt{N+1}\ (-1)^{S_2+L_2+S_2''+L_2''+2S+3S_1+S_2+2S_1''+S_2''+S''+l_0+l_2+N}\\
&\times\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^N\alpha_1S_1L_1\right)[S_2,L_2,S_2'',L_2'',S'',L'',S_1'',L_1'']^{1/2}\begin{Bmatrix}1/2 & S & S_1''\\ S_1 & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix}1/2 & S & S_1''\\ S'' & 1/2 & S_2''\end{Bmatrix}\\
&\times\begin{bmatrix}L_2 & l & L_2'' & l_0\\ L & l_2 & L_1'' & t\\ L_1 & L'' & l_1 & l_1\end{bmatrix}(l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l)R^t\,(n_0l_0n_1l_1,n_1l_1nl)\,, && (140)\\
C(\psi'',\psi') &= \sqrt{2N(N+1)}\ (-1)^{3S+2S_1'+S_3'+S_2''+3S_1''+L+L_3'+L_2''+L_1''+l+l_0+l_1+l_2+N}\\
&\times[S_2',L_2',S_3',L_3',S_1'',L_1'',S_2'',L_2'',S'',L'']^{1/2}\begin{Bmatrix}1/2 & 1/2 & S_2'\\ 1/2 & S_3' & S_2''\end{Bmatrix}\begin{Bmatrix}l_1 & l_1 & L_2'\\ l_2 & L_3' & L_2''\end{Bmatrix}\begin{Bmatrix}S_1' & S_3' & S\\ S_2'' & S'' & 1/2\end{Bmatrix}\begin{Bmatrix}L_1' & L_3' & L\\ L_2'' & L'' & l_1\end{Bmatrix}\\
&\times\sum_{\hat\alpha'\hat S'\hat L'}(-1)^{\hat L'}\ [\hat S',\hat L']^{1/2}\left(nl^{N+1}\alpha_1''S_1''L_1''\{|nl^{N-1}\alpha_1'S_1'L_1',nl^2\hat\alpha'\hat S'\hat L'\right)\begin{Bmatrix}1/2 & S'' & S_1''\\ S_1' & \hat S' & 1/2\end{Bmatrix}\begin{Bmatrix}l_0 & L'' & L_1''\\ L_1' & \hat L' & l_1\end{Bmatrix}\\
&\times\begin{Bmatrix}l & l_0 & t'\\ l_1 & l & \hat L'\end{Bmatrix}(l\|\mathbf{C}^{t'}\|l_0)(l\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(nlnl,n_0l_0n_1l_1)\,, && (141)
\end{aligned}$$

and the perturbing virtual states are defined as $\psi''=(n_0l_0^{4l_0+1}\ {}^2l_0,nl^{N+1}\alpha_1''S_1''L_1'')S''L'',(n_1l_1,n_2l_2)S_2''L_2'';SL$.

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an open n_1l_1 shell

$$\begin{aligned}
-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle &= -\sum_{\psi''}\Big(\big[A1(\psi,\psi'')+B1(\psi,\psi''+A2(\psi,\psi'')+A3(\psi,\psi'')+B3(\psi,\psi'')\big]\\
&\times\big[C1(\psi'',\psi')+D1(\psi'',\psi')+C2(\psi'',\psi')+D2(\psi'',\psi')\big]\Big), && (142)
\end{aligned}$$

where

$$\begin{aligned}
A1(\psi,\psi'') &= \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \sqrt{2}\ (-1)^{S+L+3S_2+S''+L''+S_2''+S_3''+L_3''+N} \\
&\times [S_2, L_2, S'', L'', S_2'', L_2'', S_3'', L_3'']^{1/2}\ \begin{Bmatrix} 1/2 & S'' & S_1 \\ S & S_2 & S_3'' \end{Bmatrix} \begin{Bmatrix} l_0 & L'' & L_1 \\ L & L_2 & L_3'' \end{Bmatrix} \begin{Bmatrix} S_2'' & S_3'' & 1/2 \\ S_2 & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} L_2 & l_0 & L_3'' \\ l_1 & l_1 & L_2'' \\ l_2 & t & l_2 \end{Bmatrix} \\
&\times (l_0\|\mathbf{C}^t\|l_1)(l_2\|\mathbf{C}^t\|l_2) R^t\,(n_0 l_0 n_2 l_2, n_1 l_1 n_2 l_2)\,, \qquad (143)\\
B1(\psi,\psi'') &= \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \delta(S_2, S_2'')\ \sqrt{2}\ (-1)^{3S+L+2S_1+L_2+S''+L''+L_2''+3S_3''+L_3''+l_2+N+1} \\
&\times [L_2, L_2'', S'', L'', S_3'', L_3'']^{1/2}\ \begin{Bmatrix} 1/2 & S'' & S_1 \\ S & S_2 & S_3'' \end{Bmatrix} \begin{Bmatrix} l_0 & L'' & L_1 \\ L & L_2 & L_3'' \end{Bmatrix} \begin{Bmatrix} l_1 & l_2 & L_2 \\ t & L_2'' & l_1 \end{Bmatrix} \begin{Bmatrix} L_2 & l_0 & L_3'' \\ l_2 & L_2'' & t \end{Bmatrix} \\
&\times (l_0\|\mathbf{C}^t\|l_2)(l_2\|\mathbf{C}^t\|l_1) R^t\,(n_0 l_0 n_2 l_2, n_2 l_2 n_1 l_1)\,, \qquad (144)\\
A2(\psi,\psi'') &= \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \sqrt{2}\ (-1)^{S+L+3S_2+L_2+S''+L''+3S_2''+3S_3''+L_3''+l_0+l_2+N+1} \\
&\times [S_2, L_2, S_2'', L_2'', S'', L'', S_3'', L_3'']^{1/2}\ \begin{Bmatrix} S_3'' & S & S'' \\ S_1 & 1/2 & S_2 \end{Bmatrix} \begin{Bmatrix} L_3'' & L & L'' \\ L_1 & l_0 & L_2 \end{Bmatrix} \begin{Bmatrix} S_2 & S_3'' & 1/2 \\ S_2'' & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} L_2 & L_3'' & l_0 \\ L_2'' & l_1 & l_2 \end{Bmatrix} \begin{Bmatrix} l_1 & l_0 & t \\ l_1 & l_1 & L_2'' \end{Bmatrix} \\
&\times (l_1\|\mathbf{C}^t\|l_0)(l_1\|\mathbf{C}^t\|l_1) R^t\,(n_0 l_0 n_1 l_1, n_1 l_1 n_1 l_1)\,, \qquad (145)\\
A3(\psi,\psi'') &= \sqrt{2}\ N\ (-1)^{S+L+S_2+L_2+3S_2''+L_2''+S_3''+L_3''+S''+L''+L_1+L_1''+l+l_0+l_1+l_2+N+1} \\
&\times \frac{[S_1, L_1, S_2, L_2, S_1'', L_1'', S_2'', L_2'', S_3'', L_3'', L'']^{1/2}}{[S'']^{1/2}} \begin{Bmatrix} 1/2 & 1/2 & S_2'' \\ 1/2 & S_3'' & S_2 \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & L_2'' \\ l_2 & L_3'' & L_2 \end{Bmatrix} \begin{Bmatrix} S_2 & S & S_1 \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_2 & L & L_1 \\ L'' & l_1 & L_3'' \end{Bmatrix} \\
&\times \sum_{\bar\alpha\bar S\bar L} \delta(\bar S, S'')\,\left(nl^N \alpha_1 S_1 L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \begin{Bmatrix} l & \bar L & L_1'' \\ L'' & l_0 & t \end{Bmatrix} \begin{Bmatrix} l_1 & L_1 & L'' \\ \bar L & t & l \end{Bmatrix} \\
&\times (l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_1) R^t\,(n_0 l_0 nl, nl n_1 l_1)\,, \qquad (146)\\
B3(\psi,\psi'') &= \delta(S_1, S_1'')\ \sqrt{2}\ N\ (-1)^{S+L+2S_1+S_2+L_2+3S''+3S_2''+L_2''+S_3''+L_3''+l+l_2+N+1} \\
&\times [L_1, L_1'', S_2, L_2, S_2'', L_2'', S'', L'', S_3'', L_3'']^{1/2} \\
&\times \begin{Bmatrix} S_2 & S & S_1 \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_2 & L & L_1 \\ L'' & l_1 & L_3'' \end{Bmatrix} \begin{Bmatrix} 1/2 & 1/2 & S_2'' \\ 1/2 & S_3'' & S_2 \end{Bmatrix} \begin{Bmatrix} l_1 & l_1 & L_2'' \\ l_2 & L_3'' & L_2 \end{Bmatrix} \begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1 & l_1 & t \end{Bmatrix} \\
&\times \sum_{\bar\alpha\bar S\bar L} (-1)^{\bar L}\,\left(nl^N \alpha_1 S_1 L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right) \begin{Bmatrix} t & l & l \\ \bar L & L_1'' & L_1 \end{Bmatrix} \\
&\times (l_0\|\mathbf{C}^t\|l_2)(l\|\mathbf{C}^t\|l) R^t\,(n_0 l_0 nl, n_1 l_1 nl)\,, \qquad (147)\\
C1(\psi'',\psi') &= \delta(S_1', S'')\ \delta(S_3', S_3'')\ \delta(S_2', S_2'')\ 2\sqrt{N}\ (-1)^{2S_3'+2S+2S_1''+L_3'+L+L_3''+L_1''+l+l_2+N} \\
&\times \left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\alpha_1' S_1' L_1'\right) \frac{[S_1'', L_1'', L_2', L_3', L_2'', L_3'', L'']^{1/2}}{[S_1']^{1/2}} \begin{Bmatrix} t' & L_2' & L_2'' \\ l_2 & L_3'' & L_3' \end{Bmatrix} \begin{Bmatrix} L_1' & t' & L'' \\ L_3'' & L & L_3' \end{Bmatrix} \\
&\times \begin{Bmatrix} l & L_1' & L_1'' \\ L'' & l_0 & t' \end{Bmatrix} \begin{Bmatrix} L_2' & L_2'' & t' \\ l_1 & l_1 & l_1 \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l_1\|\mathbf{C}^{t'}\|l_1) R^{t'}\,(n_0 l_0 n_1 l_1, nl n_1 l_1)\,, \qquad (148)\\
D1(\psi'',\psi') &= 2\sqrt{N}\ (-1)^{2S''+2S_1'+3S_3'+S_3''+L''+L_1'+L_2'+L_2''+L''+l+l_1+N} \left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\alpha_1' S_1' L_1'\right) \\
&\times [S_2', L_2', S_3', L_3', S'', L'', S_1'', L_1'', S_2'', L_2'', S_3'', L_3'']^{1/2} \begin{bmatrix} S_3' & 1/2 & S_3'' & 1/2 \\ 1/2 & S & 1/2 & S_1'' \\ S_2' & S_2'' & S_1' & S'' \end{bmatrix} \\
&\times \begin{bmatrix} L_1' & & L_3' & & L_2' & & l_1 & & l & \\ & L & & l_2 & & l_1 & & t' & & L_1'' \\ L'' & & L_3'' & & L_2'' & & l_1 & & l_0 & \end{bmatrix} (l_0\|\mathbf{C}^{t'}\|l_1)(l_1\|\mathbf{C}^{t'}\|l) R^{t'}\,(n_0 l_0 n_1 l_1, n_1 l_1 nl)\,, \qquad (149)\\
C2(\psi'',\psi') &= \delta(S_3', S_3'')\ \delta(\alpha_2' S_2' L_2', \alpha_2'' S_2'' L_2'')\ \delta(S_1', S'')\ \sqrt{N}\ (-1)^{L_2'+L+L_1''+l+l_2+N+1} \\
&\times \left(nl^N \alpha_1'' S_1'' L_1''\{|nl^{N-1}\alpha_1' S_1' L_1'\right) \frac{[L_3', L_3'', S_1'', L_1'', L'']^{1/2}}{[S_1']^{1/2}} \\
&\times \begin{Bmatrix} L_3' & L_3'' & t' \\ l_2 & l_2 & L_2' \end{Bmatrix} \begin{Bmatrix} L_1' & t' & L'' \\ L_3'' & L & L_3' \end{Bmatrix} \begin{Bmatrix} l_0 & l & t' \\ L_1' & L'' & L_1'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l_2\|\mathbf{C}^{t'}\|l_2) R^{t'}\,(n_0 l_0 n_2 l_2, nl n_2 l_2)\,, \qquad (150)
\end{aligned}$$

$$D2(\psi'',\psi') = \delta(\alpha_2' S_2' L_2', \alpha_2'' S_2'' L_2'')\ \sqrt{N}\ (-1)^{S''+3S_1'+3S_3'+2S_2'+3S_3''+l_0+l_2+N+1} \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1} \alpha_1' S_1' L_1'\right) \times [S_3', L_3', S'', L'', S_1'', L_1'', S_3'', L_3'']^{1/2} \begin{Bmatrix} S_1' & S & S_3' \\ S_2' & 1/2 & S_1'' \end{Bmatrix} \begin{Bmatrix} S_1'' & S'' & 1/2 \\ S_3'' & S_2' & S \end{Bmatrix} \begin{bmatrix} L_3'' & l_0 & L_3' & l \\ L_2' & L & t' & L_1'' \\ l_2 & l_2 & L'' & L_1' \end{bmatrix} \times (l_0 \| \mathbf{C}^{t'} \| l_2)(l_2 \| \mathbf{C}^{t'} \| l) R^{t'} (n_0 l_0 n_2 l_2, n_2 l_2 n l)\,, \tag{151}$$

and the perturbing virtual states are defined as $\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_1 l_1^2 \alpha_2'' S_2'' L_2'', n_2 l_2) S_3'' L_3''; SL$.

The excitation of an electron from a closed $n_0 l_0^{4l_0+2}$ shell into an open $n_2 l_2$ shell

$$-\sum_{\psi''} \langle \psi | \mathbf{G} | \psi'' \rangle \times \langle \psi'' | \mathbf{G} | \psi' \rangle = -\sum_{\psi''} \left[A1(\psi,\psi'') + A2(\psi,\psi'') + B2(\psi,\psi'') \right] \times \left[C1(\psi'',\psi') + D1(\psi'',\psi') \right], \tag{152}$$

where

$$A1(\psi,\psi'') = \delta(\alpha_1 S_1 L_1, \alpha_1'' S_1'' L_1'')\ \sqrt{2}\ (-1)^{3S+L+S_1+L_1+S''+L''+S_1''+L_1''+L_2''+l_0+l_1+l_2+N+1/2} \times [S_2, L_2, S'', L'', S_2'', L_2'', S_3'', L_3'']^{1/2} \begin{Bmatrix} S_3'' & S'' & S \\ S_1 & S_2 & 1/2 \end{Bmatrix} \begin{Bmatrix} L_3'' & L'' & L \\ L_1 & L_2 & l_0 \end{Bmatrix} \begin{Bmatrix} S_2'' & 1/2 & 1/2 \\ S_2 & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_2'' & l_0 & l_2 \\ L_2 & l_1 & L_3'' \end{Bmatrix} \begin{Bmatrix} l_2 & l_0 & t \\ l_2 & l_2 & L_2'' \end{Bmatrix} \times (l_2 \| \mathbf{C}^t \| l_0)(l_2 \| \mathbf{C}^t \| l_2) R^t (n_0 l_0 n_2 l_2, n_2 l_2 n_2 l_2)\,, \tag{153}$$

$$A2(\psi,\psi'') = \sqrt{2}\ N\ (-1)^{S+L+2S_1+L_1+3S''+L''+L_1''+l+l_0+l_1+N+1/2} \times \frac{[S_1, L_1, S_2, L_2, S_1'', L_1'', S_2'', L_2'', S_3'', L_3'', L'']^{1/2}}{[S'']^{1/2}} \begin{Bmatrix} 1/2 & S_3'' & S_2 \\ 1/2 & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_2 & L_3'' & L_2 \\ l_1 & l_2 & L_2'' \end{Bmatrix} \begin{Bmatrix} S_2 & S & S_1 \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_2 & L & L_1 \\ L'' & l_2 & L_3'' \end{Bmatrix} \times \sum_{\bar\alpha \bar S \bar L} \delta(\bar S, S'') \left(nl^N \alpha_1 S_1 L_1 \{| nl^{N-1} \bar\alpha \bar S \bar L\right) \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1} \bar\alpha \bar S \bar L\right) \begin{Bmatrix} l & \bar L & L_1'' \\ L'' & l_0 & t \end{Bmatrix} \begin{Bmatrix} l_2 & L_1 & L'' \\ \bar L & t & l \end{Bmatrix} \times (l_0 \| \mathbf{C}^t \| l)(l \| \mathbf{C}^t \| l_2) R^t (n_0 l_0 n l, n l n_2 l_2)\,, \tag{154}$$

$$B2(\psi,\psi'') = \delta(S_1, S_1'')\ \sqrt{2}\ N\ (-1)^{S+L+2S_1+S''+l+l_1+l_2+N+3/2}\ [L_1, L_1'', S_2, L_2, S_2'', L_2'', S'', L'', S_3'', L_3'']^{1/2} \times \begin{Bmatrix} 1/2 & S_3'' & S_2 \\ 1/2 & 1/2 & S_2'' \end{Bmatrix} \begin{Bmatrix} l_2 & L_3'' & L_2 \\ l_1 & l_2 & L_2'' \end{Bmatrix} \begin{Bmatrix} S_2 & S & S_1 \\ S'' & 1/2 & S_3'' \end{Bmatrix} \begin{Bmatrix} L_2 & L & L_1 \\ L'' & l_2 & L_3'' \end{Bmatrix} \begin{Bmatrix} l_2 & L'' & L_1 \\ L_1'' & t & l_0 \end{Bmatrix} \times \sum_{\bar\alpha \bar S \bar L} (-1)^{2\bar S + \bar L} \left(nl^N \alpha_1 S_1 L_1 \{| nl^{N-1} \bar\alpha \bar S \bar L\right) \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1} \bar\alpha \bar S \bar L\right) \begin{Bmatrix} l & L_1'' & \bar L \\ L_1 & l & t \end{Bmatrix} \times (l_0 \| \mathbf{C}^t \| l_2)(l \| \mathbf{C}^t \| l) R^t (n_0 l_0 n l, n_2 l_2 n l)\,, \tag{155}$$

$$C1(\psi'',\psi') = \delta(S_1', S_1'')\ \delta(S_3', S_3'')\ 2\sqrt{N}\ (-1)^{2S_1'+S_2'+S_2''+2S+3S_3'+L+L_1''+L_3''+l_0+l_1+l_2+N+1/2} \times \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1} \alpha_1' S_1' L_1'\right) \frac{[S_2', L_2', S_1'', L_1'', S_2'', L_2'', L_3', L_3'', L'']^{1/2}}{[S_1']^{1/2}} \begin{Bmatrix} 1/2 & 1/2 & S_2'' \\ S_3' & 1/2 & S_2' \end{Bmatrix} \begin{Bmatrix} L_1' & L_1'' & l \\ l_0 & t' & L'' \end{Bmatrix} \times \begin{Bmatrix} L & L'' & L_3'' \\ t' & L_3' & L_1' \end{Bmatrix} \begin{Bmatrix} l_2 & l_1 & t' \\ l_2 & L_2' & L_3' \\ L_2'' & l_1 & L_3'' \end{Bmatrix} (l_0 \| \mathbf{C}^{t'} \| l)(l_1 \| \mathbf{C}^{t'} \| l_2) R^{t'} (n_0 l_0 n_1 l_1, n l n_2 l_2)\,, \tag{156}$$

$$D1(\psi'',\psi') = 2\sqrt{N}\ (-1)^{3S+2S''+2S_1'+S_2'+S_1''+S_2''+S_3''+L''+L_1'+L_3'+l_2+N+3/2} \left(nl^N \alpha_1'' S_1'' L_1'' \{| nl^{N-1} \alpha_1' S_1' L_1'\right) \times [S_2', L_2', S_3', L_3', S'', L'', S_1'', L_1'', S_2'', L_2'', S_3'', L_3'']^{1/2} \begin{Bmatrix} S_2' & 1/2 & S_3' & S \\ 1/2 & S_2'' & S_3'' & S_1'' \\ 1/2 & 1/2 & S_1' & S'' \end{Bmatrix} \times \sum_{\lambda=|L_3'-l_0|,\dots,L_3'+l_0} (-1)^\lambda\ [\lambda] \begin{Bmatrix} \lambda & l_0 & L_3' \\ l & L_1'' & L_1' \\ L_3'' & L'' & L \end{Bmatrix} \begin{Bmatrix} l_1 & L_2' & l_1 & t' \\ L_2'' & l_2 & l_2 & \lambda \\ L_3'' & L_3' & l & l_0 \end{Bmatrix} (l_0 \| \mathbf{C}^{t'} \| l_2)(l_1 \| \mathbf{C}^{t'} \| l) R^{t'} (n_0 l_0 n_1 l_1, n_2 l_2 n l)\,, \tag{157}$$

and the perturbing virtual states are defined as $\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^N \alpha_1'' S_1'' L_1'') S'' L'', (n_1 l_1, n_2 l_2^2 \alpha_2'' S_2'' L_2'') S_3'' L_3''; SL$.

5.5.12 The configuration interaction $nl^N n_1 l_1^2 n_2 l_2 \leftrightarrow nl^{N+1} n_1 l_1 n_3 l_3$

The states ψ for $nl^N n_1 l_1^2 n_2 l_2$ configuration and ψ' for $nl^{N+1} n_1 l_1 n_3 l_3$ configuration are defined as follows:

$$\psi = (n_0 l_0^{4l_0+2}\ {}^1S, nl^N \alpha_1 S_1 L_1)\alpha_1 S_1 L_1, (n_1 l_1^2 \alpha_2 S_2 L_2, n_2 l_2) S_3 L_3; SL,$$
$$\psi' = (n_0 l_0^{4l_0+2}\ {}^1S, nl^{N+1} \alpha_1' S_1' L_1')\alpha_1' S_1' L_1', (n_1 l_1 n_3 l_3) S_2' L_2'; SL.$$

The excitation of an electron from a closed $n_0 l_0^{4l_0+2}$ shell into an open nl shell

$$-\sum_{\psi''} \langle \psi |\mathbf{G}| \psi'' \rangle \times \langle \psi'' |\mathbf{G}| \psi' \rangle =$$
$$-\sum_{\psi''} \left[A1(\psi,\psi'') + B1(\psi,\psi'') + A2(\psi,\psi'') + B2(\psi,\psi'')\right] \times \left[C(\psi'',\psi') + D(\psi'',\psi')\right], \tag{158}$$

where

$$A1(\psi,\psi'') = \delta(S_1,S'')\ \delta(S_3,S_3'')\ \delta(S_2,S_2'')\ \sqrt{N+1}\ (-1)^{2S_3+2S+2S_1''+L_2+L_3+L+L_3''+L_1''+l_0+l_2+N+1}$$
$$\times \left(nl^{N+1}\alpha_1'' S_1'' L_1'' \{|nl^N \alpha_1 S_1 L_1\right) \langle n_1 l_1^2 \alpha_2 S_2 L_2 \left\|\mathbf{U}^t\right\| n_1 l_1^2 \alpha_2'' S_2'' L_2''\rangle \frac{[S_1'', L_1'', L_3, L_3'', L'']^{1/2}}{[S_1]^{1/2}}$$
$$\times \begin{Bmatrix} t & L_2 & L_2'' \\ l_2 & L_3'' & L_3 \end{Bmatrix} \begin{Bmatrix} L_1 & t & L'' \\ L_3'' & L & L_3 \end{Bmatrix} \begin{Bmatrix} l & L_1 & L_1'' \\ L'' & l_0 & t \end{Bmatrix} (l_0\|\mathbf{C}^t\|l)(l_1\|\mathbf{C}^t\|l_1) R^t\left(n_0 l_0 n_1 l_1, n l n_1 l_1\right), \tag{159}$$

$$B1(\psi,\psi'') = 2\sqrt{N+1}\ (-1)^{2S''+2S_1+3S_3+S_3''+L_1+L_2+L_2''+L''+l+l_1+N+1} \left(nl^{N+1}\alpha_1'' S_1'' L_1'' \{|nl^N \alpha_1 S_1 L_1\right)$$
$$\times [S_2, L_2, S_3, L_3, S'', L'', S_1'', L_1'', S_2'', L_2'', S_3'', L_3'']^{1/2} \begin{bmatrix} S_3 & 1/2 & S_3'' & 1/2 \\ 1/2 & S & 1/2 & S_1'' \\ S_2 & S_2'' & S_1 & S'' \end{bmatrix}$$
$$\times \begin{bmatrix} L_1 & L_3 & L_2 & l_1 & l \\ L & l_2 & l_1 & t & L_1'' \\ L'' & L_3'' & L_2'' & l_1 & l_0 \end{bmatrix} (l_0\|\mathbf{C}^{t'}\|l_1)(l_1\|\mathbf{C}^{t'}\|l) R^{t'}\left(n_0 l_0 n_1 l_1, n_1 l_1 n l\right), \tag{160}$$

$$A2(\psi,\psi'') = \delta(S_3,S_3'')\ \delta(\alpha_2 S_2 L_2, \alpha_2'' S_2'' L_2'')\ \delta(S_1,S'')\ \sqrt{N+1}\ (-1)^{L_2+L+L_1''+l_0+l_2+N}$$
$$\times \left(nl^{N+1}\alpha_1'' S_1'' L_1'' \{|nl^N \alpha_1 S_1 L_1\right) \frac{[L_3, L_3'', S_1'', L_1'', L'']^{1/2}}{[S_1]^{1/2}}$$
$$\times \begin{Bmatrix} L_3 & L_3'' & t \\ l_2 & l_2 & L_2 \end{Bmatrix} \begin{Bmatrix} L_1 & t & L'' \\ L_3'' & L & L_3 \end{Bmatrix} \begin{Bmatrix} l_0 & l & t \\ L_1 & L'' & L_1'' \end{Bmatrix} (l_0\|\mathbf{C}^t\|l)(l_2\|\mathbf{C}^t\|l_2) R^t\left(n_0 l_0 n_2 l_2, n l n_2 l_2\right), \tag{161}$$

$$B2(\psi,\psi'') = \delta(\alpha_2 S_2 L_2, \alpha_2'' S_2'' L_2'')\ \sqrt{N+1}\ (-1)^{S''+3S_1+3S_3+2S_2+3S_3''+l+l_2+N} \left(nl^{N+1}\alpha_1'' S_1'' L_1'' \{|nl^N \alpha_1 S_1 L_1\right)$$
$$\times [S_3, L_3, S'', L'', S_1'', L_1'', S_3'', L_3'']^{1/2} \begin{Bmatrix} S_1 & S & S_3 \\ S_2 & 1/2 & S_1'' \end{Bmatrix} \begin{Bmatrix} S_1'' & S'' & 1/2 \\ S_3'' & S_2 & S \end{Bmatrix} \begin{bmatrix} L_3'' & l_0 & L_3 & l \\ L_2 & L & t & L_1'' \\ l_2 & l_2 & L'' & L_1 \end{bmatrix}$$
$$\times (l_0\|\mathbf{C}^t\|l_2)(l_2\|\mathbf{C}^t\|l) R^t\left(n_0 l_0 n_2 l_2, n_2 l_2 n l\right), \tag{162}$$

$$C(\psi'',\psi') = \delta(\alpha_1' S_1' L_1', \alpha_2'' S_2'' L_2'')\ \sqrt{2}\ (-1)^{S+L+S_2'+S''+L''+S_2''+S_3''+L_3''+l_2+l_3+N+1}$$
$$\times [S_2', L_2', S'', L'', S_2'', L_2'', S_3'', L_3'']^{1/2} \begin{Bmatrix} 1/2 & S'' & S_1' \\ S & S_2' & S_3'' \end{Bmatrix} \begin{Bmatrix} l_0 & L'' & L_1' \\ L & L_2' & L_3'' \end{Bmatrix} \begin{Bmatrix} S_2'' & S_3'' & 1/2 \\ S_2' & 1/2 & 1/2 \end{Bmatrix} \begin{Bmatrix} L_2' & l_0 & L_3'' \\ l_1 & l_1 & L_2'' \\ l_3 & t' & l_2 \end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^{t'}\|l_1)(l_3\|\mathbf{C}^{t'}\|l_2) R^{t'}\left(n_0 l_0 n_3 l_3, n_1 l_1 n_2 l_2\right), \tag{163}$$

$$D(\psi'',\psi') = \delta(\alpha_1' S_1' L_1', \alpha_1'' S_1'' L_1'')\ \delta(S_2', S_2'')\ \sqrt{2}\ (-1)^{S+L+2S_2'+L_2'+S''+L''+L_2''+S_3''+l_0+l_1+l_3+N+1}$$
$$\times [L_2', L_2'', S'', L'', S_3'', L_3'']^{1/2} \begin{Bmatrix} 1/2 & S'' & S_1' \\ S & S_2' & S_3'' \end{Bmatrix} \begin{Bmatrix} l_0 & L'' & L_1' \\ L & L_2' & L_3'' \end{Bmatrix} \begin{Bmatrix} l_1 & l_3 & L_2' \\ t' & L_2'' & l_1 \end{Bmatrix} \begin{Bmatrix} L_2' & l_0 & L_3'' \\ l_2 & L_2'' & t' \end{Bmatrix}$$
$$\times (l_0\|\mathbf{C}^{t'}\|l_3)(l_2\|\mathbf{C}^{t'}\|l_1) R^{t'}\left(n_0 l_0 n_3 l_3, n_2 l_2 n_1 l_1\right), \tag{164}$$

and the perturbing virtual states are defined as $\psi'' = (n_0 l_0^{4l_0+1}\ {}^2l_0, nl^{N+1}\alpha_1'' S_1'' L_1'') S'' L'', (n_1 l_1^2 \alpha_2'' S_2'' L_2'', n_2 l_2) S_3'' L_3''; SL$.

5.5.13 The configuration interaction $nl^N n_3l_3n_1l_1 \leftrightarrow nl^{N-1}n_3l_3n_2l_2^2$

The states ψ for $nl^N n_3l_3n_1l_1$ configuration and ψ' for $nl^{N-1}n_3l_3n_2l_2^2$ configuration are defined as follows:

$$\psi = (n_0l_0^{4l_0+2}\ {}^1S, nl^N\alpha_1S_1L_1)\alpha_1S_1L_1, (n_3l_3n_1l_1)S_2L_2)SL; SL,$$

$$\psi' = (n_0l_0^{4l_0+2}\ {}^1S, nl^{N-1}\alpha_1'S_1'L_1')\alpha_1'S_1'L_1', (n_3l_3, n_2l_2^2\alpha_2'S_2'L_2')S_3'L_3'; SL.$$

The excitation of an electron from a closed $n_0l_0^{4l_0+2}$ shell into an empty n_2l_2 shell

$$-\sum_{\psi''}\langle\psi\,|\mathbf{G}|\,\psi''\rangle\times\langle\psi''\,|\mathbf{G}|\,\psi'\rangle =$$

$$-\sum_{\psi''}\big[A1(\psi,\psi'')+B1(\psi,\psi'')+A2(\psi,\psi'')+B2(\psi,\psi'')\big]\times\big[C1(\psi'',\psi')+D1(\psi'',\psi')\big], \tag{165}$$

where

$$A1(\psi,\psi'') = \delta(S_2L_2, S_2''L_2'')\ N\ (-1)^{S+L+3S_3''+L_3''+S''+L''+L_1+L_1''+l+l_1+l_2+N}\ \frac{[S_1,L_1,S_1'',L_1'',S_3'',L_3'',L'']^{1/2}}{[S'']^{1/2}}$$
$$\times\begin{Bmatrix} S_3'' & S & S''\\ S_1 & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix} L_3'' & L & L''\\ L_1 & l_2 & L_2\end{Bmatrix}\sum_{\bar\alpha\bar S\bar L}\delta(\bar S, S'')\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)$$
$$\times\begin{Bmatrix} \bar L & l & L_1\\ l_2 & L'' & t\end{Bmatrix}\begin{Bmatrix} l & t & l_0\\ L'' & L_1'' & \bar L\end{Bmatrix}(l_0\|\mathbf{C}^t\|l)(l\|\mathbf{C}^t\|l_2)R^t\left(n_0l_0nl, nln_2l_2\right), \tag{166}$$

$$B1(\psi,\psi'') = \delta(S_1,S_1'')\ \delta(S_2L_2,S_2''L_2'')\ N\ (-1)^{S+L+2S_1+3S_3''+L_3''+3S''+l+l_0+N}\ [L_1,L_1'',S_3'',L_3'',S''L'']^{1/2}$$
$$\times\begin{Bmatrix} S_3'' & S & S''\\ S_1 & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix} L_3'' & L & L''\\ L_1 & l_2 & L_2\end{Bmatrix}\sum_{\bar\alpha\bar S\bar L}(-1)^{\bar L}\left(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\bar\alpha\bar S\bar L\right)\left(nl^N\alpha_1S_1L_1\{|nl^{N-1}\bar\alpha\bar S\bar L\right)$$
$$\times\begin{Bmatrix} t & l & l\\ \bar L & L_1 & L_1''\end{Bmatrix}\begin{Bmatrix} l_0 & L_1'' & L''\\ L_1 & l_2 & t\end{Bmatrix}(l_0\|\mathbf{C}^t\|l_2)(l\|\mathbf{C}^t\|l)R^t\left(n_0l_0nl, n_2l_2nl\right), \tag{167}$$

$$A2(\psi,\psi'') = \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ (-1)^{S+L+S_2+3S_3''+L_3''+S_2''+S''+L''+l_1+l_2+N+1}\ [S_2,L_2,S_2'',L_2'',S_3'',L_3'',S'',L'']^{1/2}$$
$$\times\begin{Bmatrix} 1/2 & 1/2 & S_2''\\ S_3'' & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix} S_3'' & S & S''\\ S_1 & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix} L_3'' & L & L''\\ L_1 & l_2 & L_2\end{Bmatrix}\begin{Bmatrix} l_3 & l_1 & L_2\\ l_1 & t & l_0\\ L_2'' & l_2 & L_3''\end{Bmatrix}$$
$$\times(l_0\|\mathbf{C}^t\|l_1)(l_1\|\mathbf{C}^t\|l_2)R^t\left(n_0l_0n_1l_1, n_1l_1n_2l_2\right), \tag{168}$$

$$B2(\psi,\psi'') = \delta(S_2,S_2'')\ \delta(\alpha_1S_1L_1,\alpha_1''S_1''L_1'')\ (-1)^{S+L+L_2+3S_3''+L_2''+S''+L''+l_0+l_1+l_3+N+1}$$
$$\times[S_3'',L_3'',L_2,L_2'',S'',L'']^{1/2}\begin{Bmatrix} S_3'' & S & S''\\ S_1 & 1/2 & S_2\end{Bmatrix}\begin{Bmatrix} L_3'' & L & L''\\ L_1 & l_2 & L_2\end{Bmatrix}\begin{Bmatrix} t & l_1 & l_1\\ l_3 & L_2 & L_2''\end{Bmatrix}\begin{Bmatrix} L_2'' & t & L_2\\ l_0 & L_3'' & l_2\end{Bmatrix}$$
$$\times(l_0\|\mathbf{C}^t\|l_2)(l_1\|\mathbf{C}^t\|l_1)R^t\left(n_0l_0n_1l_1, n_2l_2n_1l_1\right), \tag{169}$$

$$C1(\psi'',\psi') = \delta(S_1',S'')\,\delta(S_3',S_3'')\,\sqrt{2N}\,(-1)^{2S+3S_3'+2S_1''+L+L_1''+L_3''+l+N+3/2}\,\big(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\alpha_1'S_1'L_1'\big)$$
$$\times \frac{[S_2',L_2',S_1'',L_1'',S_2'',L_2'',L_3',L_3'',L'']^{1/2}}{[S_1']^{1/2}} \begin{Bmatrix} 1/2 & 1/2 & S_2'' \\ S_3' & 1/2 & S_2' \end{Bmatrix} \begin{Bmatrix} L_3' & t' & L_3'' \\ L'' & L & L_1' \end{Bmatrix} \begin{Bmatrix} l_0 & L_1'' & L'' \\ L_1' & t' & l \end{Bmatrix}$$
$$\times \begin{Bmatrix} l_3 & L_2' & L_3' \\ l_1 & l_2 & t' \\ L_2'' & l_2 & L_3'' \end{Bmatrix} (l_0\|\mathbf{C}^{t'}\|l)(l_2\|\mathbf{C}^{t'}\|l_1)R^{t'}\,(n_0l_0n_2l_2,nln_1l_1)\,, \qquad (170)$$

$$D1(\psi'',\psi') = \sqrt{2N}\,(-1)^{S+2S_1'+2S_3'+S_1''+L''+L_1'+L_2'+L_3'+l+l_2+l_3+N+3/2}\,\big(nl^N\alpha_1''S_1''L_1''\{|nl^{N-1}\alpha_1'S_1'L_1'\big)$$
$$\times [S_2',L_2',S_3',L_3',S'',L'',S_1'',L_1'',S_2'',L_2'',S_3'',L_3'']^{1/2} \begin{Bmatrix} 1/2 & & S_1'' & & 1/2 & & 1/2 & \\ & S_1' & & S'' & & S_2'' & & S_2' \\ S_3' & & S & & S_3'' & & 1/2 & \end{Bmatrix}$$
$$\times \sum_{\lambda=|l_1-l_2|,\ldots,l_1+l_2} (-1)^{\lambda}\,[\lambda] \begin{Bmatrix} l_3 & l_1 & L_2'' \\ l_2 & L_3'' & \lambda \end{Bmatrix} \begin{bmatrix} \lambda & & l_1 & & l_0 & & L'' & & L_3'' & \\ & l_2 & & t' & & L_1'' & & L & & l_3 \\ L_2' & & l_2 & & l & & L_1' & & L_3' & \end{bmatrix}$$
$$\times (l_0\|\mathbf{C}^{t'}\|l_1)(l_2\|\mathbf{C}^{t'}\|l)R^{t'}\,(n_0l_0n_2l_2,n_1l_1nl)\,, \qquad (171)$$

and the perturbing virtual states are defined as

$$\psi'' = (n_0l_0^{4l_0+1}\ {}^2l_0, nl^N\alpha_1''S_1''L_1'')S''L'', ((n_3l_3,n_1l_1)S_2''L_2'', n_2l_2)S_3''L_3''; SL.$$

6 Results

This approach was first used for the analysis of the configuration system $(5\text{d}+6\text{s})^N$ of the lanthanum atom [26], then it was applied to the atomic structure of the tantalum atom [29], the scandium ion [35], the titanium ion [36] and the niobium atom [30]. Recently, we reported how to detect the isomeric state $I = (3/2)^+$ in ^{229}Th by the means of the laser induced fluorescence method [28]. To answer this question we considered a system of 70 even configurations of Th^+. The system had 3804 energy eigenvalues, the same number of predicted A constants and 3486 B constants. In our procedure, we used all the experimental data known up to day, *i.e.* the values of 316 electronic energy levels, 11 A and 10 B *hfs* constants. In the fine structure analysis we used 111 independent parameters. The mean difference between the experimental and calculated energies amounts to $79\,\text{cm}^{-1}$. For the hyperfine structure A and B constants, the corresponding values are 13 and 71 MHz, respectively.

The effects of the excitations of one electron from a closed shell to an open shell were considered as the configuration interaction effects (C) and electrostatically correlated spin-orbit interaction (CSO). Thus, the appropriate parameters of the second order perturbation theory were determined. Moreover, we presented the results of the semi-empirical fine and hyperfine structure analysis for Th ion, together with the predictions of the energy values and *hfs* constants for the levels up to approx. $68000\,\text{cm}^{-1}$. A selection of these results is given in table 1. Calculation details and a more extensive comparison to the experiment are contained in [28].

7 Conclusions

The fine structure analysis should be carried out on the broadest possible configuration basis. The derived and programmed formulae allowed us to analyse the spectra of the elements with complex configurations systems, including also configurations with open nf shells. As a result of our semi-empirical approach, we are able to predict the positions of new energy levels, and determine the intermediate coupling wave functions, which is necessary to understand the strength of the transitions or the observed hyperfine structure splittings. Our analysis clearly demonstrates that obtaining the precise wave functions is impossible without considering the contribution of the second order perturbation theory to electrostatic interactions.

The results for the *fs* and *hfs* of multiconfigurational systems show that a close collaboration between the experimental work and the semi-empirical calculations can be very beneficial for the investigations of the structure and spectra of complex atoms.

Table 1. Comparison of the experimental and calculated energy values [cm^{-1}] and *hfs* A and B constants [MHz] for Th^+ even configuration system.

E_{exp}	E_{calc}	%	Main comp.	%	Sec. comp.	$g_{J_{calc}}$	$g_{J_{exp}}$	A_{exp}	A_{calc}	B_{exp}	B_{calc}
$J = 5/2$											
1521.896	1582	65.86	$6d^2(^3F)7s\ ^4F$	15.35	$6d^2(^1D)7s\ ^2D$	1.069	1.076	477	499	240	240
4113.359	4161	36.37	$6d\ 7s^2\ ^2D$	26.69	$6d^2(^3F)7s\ ^4F$	1.165	1.163	210	190	780	762
8605.841	8578	43.99	$6d^2(^3F)7s\ ^2F$	15.02	$6d^2(^3P)7s\ ^4P$	1.062	0.986		−4		548
9061.103	9078	56.62	$6d^2(^3P)7s\ ^4P$	20.39	$6d^2(^3F)7s\ ^2F$	1.348	1.419		535		−556
9400.964	9365	72.20	$6d^3\ ^4F$	13.06	$6d^2(^3F)7s\ ^2F$	1.027	1.034		−156		−209
13250.509	13179	39.33	$6d^2(^1D)7s\ ^2D$	18.43	$6d\ 7s^2\ ^2D$	1.252	1.245		478		18
15786.985	15750	85.88	$6d^3\ ^4P$	4.14	$6d^3\ ^2D$	1.563	1.571		−331		1735
20158.739	20148	59.53	$6d^3\ ^2D$	13.05	$6d^2(^1D)7s\ ^2D$	1.199	1.190		155		−1230
22106.433	22141	61.33	$6d^3\ ^2F$	8.23	$6d^2(^3F)7s\ ^2F$	0.937	0.920		204		2456
26488.647	26475	35.86	$5f\ 7s7p\ (^3P)\ ^4G$	23.08	$5f\ 7s7p\ (^3P)\ ^4F$	0.825	0.776		84		824
27593.968	27609	33.94	$5f^2(^3F)7s\ ^4F$	26.23	$5f^2(^3F)7s\ ^2F$	0.968	0.963		741		−736
28026.349	28060	55.47	$6d^3\ ^2D$	13.26	$6d^3\ ^2F$	1.149	1.130		19		1381
28823.653	28826	27.53	$5f\ 7s7p\ (^3P)\ ^4G$	19.63	$5f\ 7s7p\ (^3P)\ ^4F$	0.929	0.987		207		1799
29345.896	29553	29.66	$5f^2(^3F)7s\ ^2F$	28.63	$5f^2(^3F)7s\ ^4F$	0.930	0.935		−223		−213
31259.296	31275	21.91	$5f\ 6d7p\ (^3F)\ ^4G$	13.84	$5f^2(^3F)7s\ ^2F$	0.775	0.781		212		176
31754.210	31828	40.49	$5f\ 7s7p\ (^3P)\ ^2F$	12.17	$5f\ 7s7p\ (^3P)\ ^4F$	0.942	0.948		−374		596
33730.934	33648	19.51	$5f^2(^1D)7s\ ^2D$	7.85	$5f\ 6d7p\ (^3F)\ ^2D$	1.054	1.031		445		−924
34174.542	34189	25.34	$5f\ 7s7p\ (^3P)\ ^4D$	19.81	$5f\ 7s7p\ (^3P)\ ^4F$	1.025	0.986		272		28
34543.556	34473	18.47	$5f\ 6d7p\ (^3D)\ ^4G$	8.17	$5f^2(^1D)7s\ ^2D$	0.937	1.003	366.1	366	−90	−1
35741.297	35702	19.75	$5f\ 6d7p\ (^3F)\ ^4G$	19.72	$5f^2(^3F)6d\ ^4G$	0.788	0.954		169		−255
36065.740	36252	16.48	$5f^2(^3F)6d\ ^4G$	10.11	$5f^2(^1D)7s\ ^2D$	1.041	0.887		296		−474
37465.458	37390	15.28	$5f\ 6d7p\ (^3D)\ ^4D$	6.58	$5f\ 6d7p\ (^3F)\ ^4G$	1.063	1.048		105		24
37945.109	37980	20.73	$5f\ 7s7p\ (^1P)\ ^2F$	11.47	$5f^2(^3P)7s\ ^4P$	1.036	0.893		181		−526
38105.072	38201	15.93	$5f\ 7s7p\ (^1P)\ ^2F$	13.29	$5f^2(^3P)7s\ ^4P$	1.135	1.172		179		−402

ME thanks Poznań University of Technology for financial support within the project 06/63/DSPB/0315. JD and JR thank Poznań University of Technology for financial support within the project 04/45/DSPB/0135.

References

1. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **130**, 14 (2015) DOI: 10.1140/epjp/i2015-15014-8.
2. L. Armstrong Jr., *Theory of the Hyperfine Structure of Free Atoms* (Willey-Interscience, New York, 1971).
3. I. Lindgren, J. Morrison, *Atomic Many-Body Theory* (Springer-Verlag, Berlin Heidelberg New York, 1982).
4. L. Armstrong Jr., S. Feneuille, Phys. Rev. **173**, 58 (1968) DOI: 10.1103/PhysRev.173.58.
5. L. Armstrong Jr., S. Feneuille, Adv. At. Mol. Phys. **10**, 1 (1974) DOI: 10.1016/S0065-2199(08)60346-2.

6. J. Dembczyński, G. Szawioła, M. Elantkowska, E. Stachowska, J. Ruczkowski, Phys. Scr. **54**, 444 (1996) DOI: 10.1088/0031-8949/54/5/004.
7. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Phys. Scr. **59**, 49 (1999) DOI: 10.1238/Physica.Regular.059a00049.
8. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **130**, 15 (2015) DOI: 10.1140/epjp/i2015-15015-7.
9. M. Elantkowska, J. Ruczkowski, J. Dembczyński, Eur. Phys. J. Plus **130**, 83 (2015) DOI: 10.1140/epjp/i2015-15083-7.
10. R.E. Tress, Phys. Rev. **83**, 756 (1951) DOI: 10.1103/PhysRev.83.756.
11. R.E. Tress, Phys. Rev. **84**, 1089 (1951) DOI: 10.1103/PhysRev.84.1089.
12. R.E. Tress, Phys. Rev. **85**, 382 (1952) DOI: 10.1103/PhysRev.85.382.
13. K. Rajnak, B.G. Wybourne, Phys. Rev. **132**, 280 (1963) DOI: 10.1103/PhysRev.132.280.
14. B.G. Wybourne, J. Math. Phys. **4**, 354 (1963) DOI: 10.1063/1.1703961.
15. B.G. Wybourne, *Spectroscopic properties of Rare Earths* (Interscience, New York, 1965).
16. B.R. Judd, Phys. Rev. **141**, 4 (1966) DOI: 10.1103/PhysRev.141.4.
17. S. Feneuille, J. Phys. **28**, 61 (1967) DOI: 10.1051/jphys:0196700280106100.
18. S. Feneuille, J. Phys. **28**, 315 (1967) DOI: 10.1051/jphys:01967002803-4031500.
19. S. Feneuille, J. Phys. **28**, 497 (1967) DOI: 10.1051/jphys:01967002805-6049700.
20. S. Feneuille, J. Phys. **28**, 701 (1967) DOI: 10.1051/jphys:01967002808-9070100.
21. J. Dembczyński, Physica C **100**, 105 (1980) DOI: 10.1016/0378-4363(80)90067-4.
22. J. Dembczyński, Physica C **141**, 219 (1986) DOI: 10.1016/0378-4363(86)90276-7.
23. W. Ertmer, U. Johann, J. Dembczyński, Z. Michalski, Z. Phys. D **2**, 67 (1986) DOI: 10.1007/BF01437244.
24. R. Aydin *et al.*, Z. Phys. D **15**, 281 (1990) DOI: 10.1007/BF01437170.
25. J. Dembczyński, G.H. Guthoehrlein, E. Stachowska, Phys. Rev. A **48**, 2752 (1993) DOI: 10.1103/PhysRevA.48.2752.
26. J. Dembczyński, M. Elantkowska, B. Furmann, J. Ruczkowski, D. Stefańska, J. Phys. B: At. Mol. Opt. Phys. **43**, 065001 (2010) DOI: 10.1088/0953-4075/43/6/065001.
27. R.D. Cowan, *The Theory of Atomic Structure and Spectra* (Berkeley University of California Press, Berkeley, 1981).
28. J. Dembczyński, M. Elantkowska, J. Ruczkowski, Phys. Rev. A **92**, 012519 (2015) DOI: 10.1103/PhysRevA.92.012519.
29. B. Arcimowicz, J. Dembczyński, P. Głowacki, J. Ruczkowski, M. Elantkowska, G. Guthöhrlein, L. Windholz, Eur. Phys. J. ST **222**, 2085 (2013) DOI: 10.1140/epjst/e2013-01988-6.
30. J. Dembczyński, M. Elantkowska, J. Ruczkowski, I.K. Öztürk, A. Er, F. Güzelçimen, Gö. Başar, S. Kröger, J. Phys. B: At. Mol. Opt. Phys. **48**, 015006 (2015) DOI: 10.1088/0953-4075/48/1/015006.
31. R.D. Cowan, available `https://www.tcd.ie/Physics/people/Cormac.McGuinness/Cowan/`.
32. H.A. Jahn, J. Hope, Phys. Rev. **93**, 318 (1954) DOI: 10.1103/PhysRev.93.318.
33. R.J. Ord-Smith, Phys. Rev. **94**, 1227 (1954) DOI: 10.1103/PhysRev.94.1227.
34. A.P. Yutsis, I.B. Levinson, V.V. Vanagas, *Mathematical Apparatus of the Angular Momentum Theory* (Vilnius 1960) (English translation: Israel Program for Scientific Translations, Jerusalem 1962; Gordon and Breach, New York, 1963).
35. J. Ruczkowski, M. Elantkowska, J. Dembczyński, J. Quant. Spectrosc. Radiat. Transfer **145**, 20 (2014) DOI: 10.1016/j.jqsrt.2014.04.018.
36. J. Ruczkowski, M. Elantkowska, J. Dembczyński, J. Quant. Spectrosc. Radiat. Transfer **149**, 168 (2014) DOI: 10.1016/j.jqsrt.2014.08.010.