CALCULATION OF ENERGY SHIFTS FOR DEGENERATE LEVELS OF MULTI-ELECTRON ATOMS

B. M. Davidovich*, V. G. Levich,
and V. V. Tolmachev

UDC 539.184

The use of the mathematical methods of the quantum field theory for the study of a number of perturbation theories dealing with multi-electron atoms has proved quite fruitful [1-3]. On the one hand it has made possible numerical calculations of the energy, probability exchange, etc. [2-4] and on the other it has been used for the interpretation of atomic spectra [5, 6].

The complete procedure has been thoroughly reported [3] in which the energy shifts for various degenerate levels of multi-electron atoms have been calculated. This procedure depends upon the determination of the energy shifts ΔE through the solution of a specifically constructed system of secular equations with a secular matrix M, the matrix elements of which are found from the sum of the contributions from the corresponding atomic Faymanov diagrams.

In this note we describe how to carry out the procedure for the compilation of the contributions from these diagrams using as a specific example the calculation of ΔE for the ^2P term of configurations $1s^22s^22p$ and $1s^22p^3$ of the boron atom, a diagram of the second order; it is always necessary to perform the preliminary details of the general procedure before doing concrete calculations of the energy shifts for any term of every configuration. If the electron interaction is not taken into account, then the two states $1s^22s^22p\ ^2P$ and $1s^22p^3\ ^2P$ have the same energy, i.e., in the null approximation the ^2P term is doubly degenerate.

It is useful to express the energy shifts for the specified state in the form

$$\begin{aligned} \Delta E_1(1s^22s^22p\,{}^2P) &= \Delta E_0(1s^2\,{}^1S) + \Delta E_1'(2s^22p\,{}^2P), \\ \Delta E_2(1s^22p^3\,{}^2P) &= \Delta E_0(1s^2\,{}^1S) + \Delta E_2'(2p^3\,{}^2P), \end{aligned}$$

where $\Delta E(1s^2\ ^1S)$

$$\begin{pmatrix} M(s^2p;\ s^2p\,|\,\Delta E')\, M(s^2p;\ \ p^3\,|\,\Delta E') \\ M(p^3;\ s^2p\,|\,\Delta E')\, M(p^3;\ p^3\,|\,\Delta E') \end{pmatrix} \begin{pmatrix} C\,(s^2p) \\ C\,(p^3) \end{pmatrix} = \Delta E' \begin{pmatrix} C\,(s^2p) \\ C\,(p^3) \end{pmatrix},$$

where the detailed symbols refer to the matrix elements of the matrix M(ΔE').

We will show how to calculate the matrix elements of the secular matrix M(ΔE') using as an example the element $M(s^2p;\ p^3|\Delta E')$. It is found as the sum of the contributions from the corresponding diagrams. The diagrams in each order are distinguished by the number of outer lines (2, 4, 6, etc.). The number of outer lines must always be less than or equal to twice the number of electrons in the outer shell of the configuration; for example, in the given case, diagrams only with 2, 4, and 6 outer lines are considered. The principle of compiling the contribution from the diagrams, the number of outer lines of which is equal to twice the number of electrons in the outer shell, is illustrated below. The contribution from the diagrams with the number of outer lines less than twice the number of electrons is expressed through the contributions from one and the same diagram and for the case when twice the number of electrons in the outer shell coincides with the number of outer lines.

---

*Corresponding Member, Academy of Sciences of the USSR.

Lomonosov State University, Moscow. Translated from Doklady Akademii Nauk SSSR, Vol. 186, No. 1, pp. 124-127, May, 1969. Original article submitted January 24, 1969.

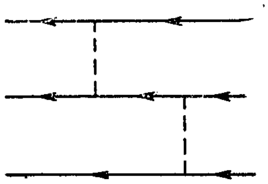


Fig. 1

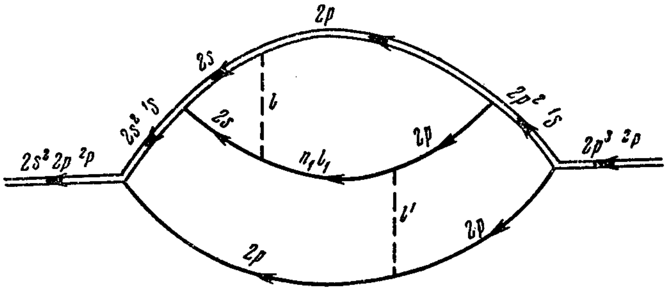


Fig. 2

For example, for any diagram of the second order with four outer lines (we will characterize the contribution from it as M_O) we have in our case

$$M_D(s^2p,\ p^3|\Delta E') =$$

$$g(s^2p\,^2P;\ s^2\,^1S;\ p^2\,^1S,\ p^3\,^2P)\,M_D(s^2\,^1S,\ p^2\,^1S|\Delta E').$$

The coefficients g do not depend on the interaction and are calculated through the corresponding genealogical coefficients; tables of g coefficients must be set up beforehand [3].

We will now consider the diagram shown in Fig. 1 and work out the contribution from it to the matrix element $M(s^2p;\ p^3|\Delta E')$ which we are considering. This contribution is the sum of the product of the factors drawn up from the following three diagrams: radial, orbital moment, and spin (cf. Figs. 2, 3, and 4).

Contribution from diagram = Σ radial factor × orbital moment factor × spin factor.

The summation is carried out: (1) using all possible arrangements of moments on the lines of the diagram; (2) using all indices of the intermediate terms; (3) using double indices $n_1 l_1$; 4) using indices l and l' from 0 to ∞.

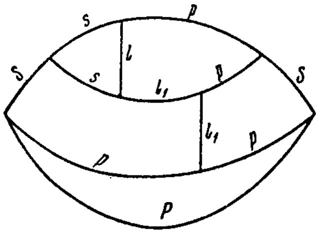


Fig. 3

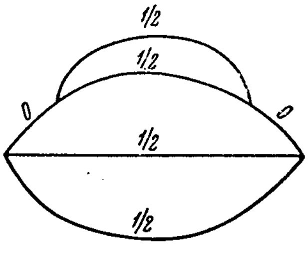


Fig. 4

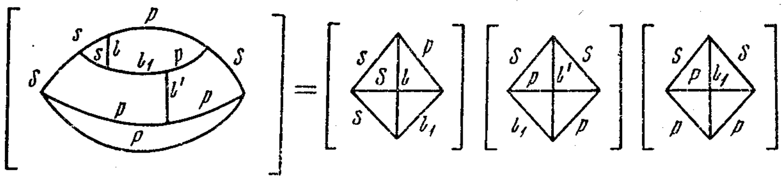
The radial diagram with the indices arranged on it is shown in Fig. 2. The arrangement of the indices on the diagram is ambiguous; for example, on the left intermediate double line we may put other indices 2s2p $^3P'$, 2s2p $^1P'$. The arrangement of the indices on the other lines of the diagram will change correspondingly. When we compile the contribution for the diagram with the given arrangement of indices, we must sum it over all possible arrangement of indices including all indices of intermediate terms standing on the intermediate double lines.

The radial factor with the appropriate diagram is drawn in Fig. 2 with the arrangement of indices as shown in the diagram and after some simplification has been made, is of the form

$$-18R_1(2020;\ n_1121)\,R_0\,(n_1121;\ 2121)\,\frac{1}{\varepsilon_{n_1}-\Delta E'}\times(s^2p\,^2P\{|\,s^2\,(^1S)\,p\,^2P)\,(p^2\,(^1S)\,p\,^2P\,|\}p^3\,^2P),$$

where $\varepsilon_{n_1} = -1/2\,n_1^2$. The radial integrals are compared with the quadruple vertices and genealogical coefficients with the triple vertices.

The orbital moment diagram is depicted in Fig. 3. It is obtained from the radial in the following way: (1) we join the outer double lines; (2) we replace all double and dashed lines by single lines; (3) we leave on all lines those indices of moments which stood on the corresponding lines in the radial diagram. The rules for the combination of contributions from the orbital moment diagrams are the usual ones [7]; we shall not dwell on them. Taking advantage of the fact that we may divide the diagram in Fig. 3 in two places by three lines we readily obtain for the orbital moment factor from the given arrangement of indices of moments that



$$=\begin{Bmatrix} s & p & l \\ l_1 & s & s \end{Bmatrix}\begin{Bmatrix} s & s & l' \\ p & l_1 & p \end{Bmatrix}\begin{Bmatrix} s & s & l' \\ p & p & p \end{Bmatrix}$$

The corresponding spin diagram is shown in Fig. 4. It is obtained from the radial as a result of the following transformations: (1) we reject all dashed lines and change all double lines into single ones; (2) on all lines we put those spins which stand on the corresponding lines of the radial diagram. The principle of drawing up contributions from the spin diagrams is the same as that for the orbital moment diagrams [7]. After some simplification, we may obtain at once for the spin diagram, shown in Fig. 4, that the contribution from it is equal to two.

We will now write the final contribution for the diagram in Fig. 1 in the matrix element $M(s^2p,\ p^3|\Delta E')$

$$\frac{28}{3}\sum_{n_1\in g_0} R\,(2020;\ n_1121)\,R_0\,(n_1121;\ 2121)\,\frac{1}{\varepsilon_{n_1}-\Delta E'}$$
$$+\frac{\sqrt{2}}{27}(-25+5\sqrt{5}+3\sqrt{3}+15\sqrt{15})\sum_{n_1\in g_0} R_1\,(2021;\,n_1021)\,R_1\,(n_1020;\,2121)$$
$$\times\frac{1}{\varepsilon_{n_1}-\Delta E'}+\frac{\sqrt{2}}{9}\,(29+5\sqrt{5}-9\sqrt{3}-15\sqrt{15})\sum_{n_1\in g_0} R_0\,(2120;\quad n_1021)$$
$$\times R_1\,(n_1020;\ 2121)\,\frac{1}{\varepsilon_{n_1}-\Delta E'}\,.$$

Here already are the expansions of the genealogical coefficients. g_0 is the combination of the unoccupied single electron state, including in itself both the state of discrete spectra and also the state of continuous spectra.

The expression is obtained as a particular case from the general expression for the contribution from the diagram in Fig. 1 for the matrix element

$$M\,(n_0l_an_0l_bn_0l_cSL;\ \ n_0l_dn_0l_mn_0l_kSL\,|\,\Delta E'),$$

where $n_0l_an_0l_bn_0l_c$ and are the arbitrary interacting three electron configurations and SL is the term of these configurations.

We write this contribution

$$(-1)^{S+{}^{3}/_{2}+L-{}^{1}/_{2}\,(l_a+l_b+l_c+l_d+l_m+l_k)}\,\delta_{S^{1}/_{2}\,{}^{1}/_{2}}\,6\sum_{\substack{S'L'\\ S'''\ L'''}}\ \sum_{n_1l_1\in g_0}\ \sum_{ll'} R_l\,(n_0l_an_0l_b;\ \ n_1l_1n_0l_d)$$
$$\times R_{l'}\,(n_1l_1n_0l_c;\ n_0l_mn_0l_k)\,[l_al_dl]\,[l_bl_1]\,[l_1l_kl']\,[l_cl_ml']$$
$$\times\,(l_al_bl_cSL\{\,|\,l_al_b\,(S'L')\,l_cSL)\,(l_al_bS'L'\,\{\,|\,l_a\,(S''L'')\,l_bS'L'')$$
$$\times(l_d\,(S^{\mathrm{IV}}L^{\mathrm{IV}})\,l_kS'''L'''\,|\}\,l_dl_kS'''L''')\,(l_dl_k\,(S'''L''')\,l_mSL\,|\}\,l_dl_kl_mSL)$$
$$\times(2l_1+1)\sqrt{2l_a+1}\sqrt{2l_b+1}\sqrt{2l_c+1}\sqrt{2l_d+1}\sqrt{2l_k+1}\sqrt{2l_m+1}$$
$$\times\sqrt{2L'+1}\sqrt{2S'+1}\sqrt{2L'''+1}\sqrt{2S'''+1}\,\frac{1}{\varepsilon_{n_1}-\Delta E'}\,\delta_{S'S'''}\delta_{{}^{1}/_{1}{}^{1}/_{2}}$$
$$\times\begin{Bmatrix}l_al_dl\\ l_1l_bL'\end{Bmatrix}\begin{Bmatrix}L'L'''l'\\ l_kl_1l_d\end{Bmatrix}\begin{Bmatrix}L'L'''l'\\ l_ml_cL\end{Bmatrix}.$$

The first summation is derived for all possible arrangements of the indices of the moments. The expression in square brackets denotes 3-j Vigner coefficients with zero projection of moments.

To carry out numerical calculations according to the perturbation theory to the second order inclusively by the process described above, it is necessary to compile standard tables of contributions for all diagrams of the first and second order.

LITERATURE CITED

1. B. R. Judd, Second Quantization and Atomic Spectroscopy, Baltimore (1967).
2. H. P. Kelly, Phys. Rev., 131, 684 (1963); H. P. Kelly, Phys. Rev., 136, B897 (1964); H. P. Kelly, Phys. Rev., 144, 39 (1966).

3. V. V. Tolmachev, Advances in Chemical Physics, 14 (1968).
4. U. I. Safronova, A. N. Ivanova, and V. V. Tolmachev, Litovsk. Fiz. Sborn., 7, 303 (1967); U. I. Safronova and V. V. Tolmachev, Teoretich. i Éksp. Khim., 3, 571 (1967); U. I. Safronova and V. V. Tolmachev, ibid., 3, 579 (1967).
5. L. N. Ivanov and V. V. Tolmachev, Izv. Vyssh. Uchebn. Zaved, Tomsk, 12, (1968).
6. B. R. Judd, Advances in Chemical Physics, 14 (1968).
7. A. P. Yutsis, I. B. Levinson, and V. V. Vanagas, Mathematical Apparatus of the Moment Theory of Quantitative Movement [in Russian], Vilnus (1960).