Preliminary evaluation of the contribution of admixed configurations

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Configuration interaction is currently the main and the most universal method for taking into account correlation effects in calculation of energy spectra and other characteristics of many-electron atoms. If the high accuracy of the energy of the atomic state under study is required and the multiconfigurational wave function describing adequately this state is necessary, one needs superposition of a great number of admixed configurations. This requires formation of quite an extensive radial orbital basis set with a wide interval of orbital quantum numbers. Extension of the radial orbital basis set used leads in its turn to fast growth of possible virtual excitations, i.e. the number of possible admixed configurations. In this case, the range of energy operator matrices also grows very rapidly. Calculation and diagonalization of such extensive energy matrices may pose quite a difficult task even for powerful modern computers. Thus, there appears a problem of selecting the most important admixed configurations from their whole set and separating those who may be neglected. Therefore, we encounter the problem of evaluating the role and selecting the most significant admixed configurations in each particular case, i.e. for a certain individual configuration under study and a given radial orbital basis set. In order to evaluate the averaged influence of a particular admixed configuration, one should average the corrections written in the second order of the many body perturbation theory over all the terms of the configuration under study:

$$
\begin{aligned}
\delta E\left(K, K'\right) &= \sum_{TLS} (2L+1)(2S+1) \sum_{T'} \frac{\langle KTLS|\hat{H}|K'T'LS\rangle^2}{\langle K'T'LS|\hat{H}|K'T'LS\rangle - \langle KTLS|\hat{H}|KTLS\rangle} \\
&\approx \frac{\sum_{TLST'} (2L+1)(2S+1)\langle KTLS|\hat{H}|K'T'LS\rangle^2}{E\left(K', K\right) \sum_{TLS} (2L+1)(2S+1)}.
\end{aligned}
$$

There $\hat{H}$ denotes the non-relativistic energy operator. The analytical expressions for sums of squares of interconfigurational matrix elements presented in the numerator are rather simple [1]. $E(K', K)$ denotes the averaged energy difference between mixing configurations. The simplest way to evaluate $E(K', K)$ is to use the well-known analytical formula for the configuration

energy averaged over its all terms:

$$\bar{E}\left(K',K\right) \;=\; \frac{\sum\limits_{T'L'S'} \left(2L'+1\right)\left(2S'+1\right)\langle K'T'L'S'|\hat{H}|K'T'L'S'\rangle^2}{\sum\limits_{T'L'S'} \left(2L'+1\right)\left(2S'+1\right)} \;-$$

$$\frac{\sum\limits_{TLS} \left(2L+1\right)\left(2S+1\right)\langle KTLS|\hat{H}|KTLS\rangle^2}{\sum\limits_{TLS} \left(2L+1\right)\left(2S+1\right)}\;.$$

The results of the preliminary evaluations of the averaged energy corrections obtained by this way were successfully used in many calculations and show high accuracy in the most cases. On the other hand last treatments show that it is possible to get a better agreement with results obtained by the real diagonalizing of the energy matrices. For this purpose it is necessary to describe more exactly the energy difference $E(K',K)$. It may be done if interconfigurational matrix elements are included in the averaging:

$$\tilde{E}\left(K',K\right) =$$

$$\frac{\sum\limits_{LSPP'} \left(2L+1\right)\left(2S+1\right)\langle KPLS|\hat{H}|K'P'LS\rangle^2 \left(\langle K'P'LS|\hat{H}|K'P'LS\rangle^{-}\langle KPLS|\hat{H}|KPLS\rangle\right)}{\sum\limits_{LSPP'} \left(2L+1\right)\left(2S+1\right)\langle KPLS|\hat{H}|K'P'LS\rangle^2}\;.$$

This expression is written within the intermediate coupling scheme, in which the operator $\hat{H}$ is diagonal with respect to the intermediate quantum numbers P within each configuration. Analytical expressions for such energy difference are derived for all possible types of the admixed configurations. Of course, these expressions are more complicated than the difference of the ordinary averaged energies, but it is not a problem to use them in computational calculations. Usage of this energy difference allows us to get very good agreement between the preliminary evaluations and the averaged results from diagonalization of energy matrices.

[1] S. Kucas, V. Jonauskas and R. Karazija, *Physica Scripta* **55** 667 (1997).