**INTERMEDIATE HAMILTONIAN COUPLED CLUSTER METHOD: EVEN MORE ACCURATE TRANSITION ENERGIES OF HEAVY ATOMS**

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The relativistic Fock-space coupled cluster method has been used by us in recent years to calculate energy levels of heavy and super-heavy atoms and molecules. Based on the Dirac-Coulomb-Breit Hamiltonian and including correlation at the CCSD level, the method gave excellent agreement (usually better than 0.1 eV) with experimental transition energies (excitation energies, ionization potentials, electron affinities) when the latter were known, and made possible reliable prediction of these properties for super-heavy elements. More recently, an intermediate Hamiltonian FSCC has been developed, which allows the use of much larger $P$ (model) spaces than before and minimizes intruder state problems, thereby extending greatly the domain of applicability of the method and giving even better accuracy [1].

The intermediate Hamiltonian method has been proposed by Malrieu [2] in the framework of degenerate perturbation theory. The basic idea is the partitioning of $P$ into a main $P_m$ and intermediate $P_i$ serving as buffer, with concomitant definition of two types of wave and excitation (or cluster) operators. Malrieu's formulation included the dangerous $P_m \rightarrow P_i$ excitations in fourth and higher orders, and could not therefore be implemented in coupled cluster methodology. We devised a scheme which eliminates this problem and applied it to a number of systems. Examples to be presented will include:

- Excitation energies of barium and radium, where the IH method made accessible many levels not available before and increased accuracy by factors of 2–5.
- Electron affinities of alkali atoms (Na to element 119), where known values (for Na, K, Rb and Cs) were reproduced within 1% or 5 meV, making possible reliable predictions for Fr and E119, not known experimentally. The relativistic increase in the EAs of these two elements, reversing the trend of EAs becoming smaller as the atom gets heavier, will be discussed.
- Excitation energies of Xe and Rn, which cannot be calculated at all by FSCC, whereas the IH method gave dozens of levels with average accuracy of 0.5–0.6%.

# References

[1] A. Landau, E. Eliav, and U. Kaldor, Chem. Phys. Lett. **313**, 399 (1999); A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor, J. Chem. Phys. **113**, 9905 (2000); A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor, J. Chem. Phys. **114**, 2977 (2001); A. Landau, E. Eliav, and U. Kaldor, Adv. Quantum Chem. in press.

[2] J.-P. Malrieu, Ph. Durand, and J.-P. Daudey, J. Phys. A **18**, 809 (1985).