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Approximate molecular relativistic Dirac-Coulomb calculations using a simple Coulombic correction

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Abstract. A simple point-charge model is used to correct molecular four-component Dirac-Coulomb calculations which neglect two-electron integrals over the small components of the wave function. The calculated valence properties show no degeneration relative to the full calculation, while a speed-up factor of 3 is obtained.

Key words: Relativistic calculations – Spectroscopic constants

1 Introduction

Molecular calculations based on the four-component Dirac-Coulomb Hamiltonian are computationally demanding. One reason is that, since the spin-orbit interaction is taken into account variationally, the degrees of freedom due to electron spin cannot be integrated out. The main reason why four-component calculations are more expensive than their two- or one-component counterparts is, however, due to the additional basis set that is needed to describe the small components of the orbitals. The kinetic balance condition [1] dictates use of a basis set that contains both functions with lower $(\ell - 1)$ and functions with higher $(\ell + 1)$ angular momentum than the functions used to expand the large component. Because of the higher degeneracy of the $(\ell + 1)$ basis functions, especially when these are expressed using primitive Cartesian type functions, the small component basis set can become two times larger than the corresponding large component basis set.

The rate-determining step in Dirac-Coulomb Hartree-Fock calculations is thereby the evaluation and handling of two-electron integrals $\mathbf{I}^{SS,SS}$ over four small component-type basis functions. Ironically, this class of integrals contributes formally only in the order of α^4 to the electronic energy of the system. Many authors [2–5] have suggested neglecting this class of integrals entirely, either in the initial stages of an iterative calculation on a heavy system or throughout the whole procedure. This type of approximation has mostly been applied to bond properties – length, vibrational frequency and dissociation energy – for molecules where bonds are formed between a heavy and a light atom. The results showed good agreement with the full calculations.

Complete neglect of integrals with four small component labels does, however give spurious results when the occupation of the small component functions is non-negligible in both atoms. For a bond between two heavy atoms, the discrepancies between the full calculation and a calculation in which the $\mathbf{I}^{SS,SS}$ class is neglected, become very large. This is demonstrated for diatomic astatine where the calculated spectroscopic constants obtained with the approximate calculation contain large errors, i.e. 10 pm in the r_c, and a D_e that is three times too large (see Tables 1 and 2). The cause and remedy of this discrepancy are explained below.

2 Theory

The Dirac-Coulomb energy of a four-component wave function that is expanded in separate one-particle basis sets for the large (L) and small (S) components can be written in terms of matrix representations of the operators as

$$\begin{aligned} E^{DC} = {} & \mathbf{D}^{LL} \bullet \mathbf{V}^{LL} + \mathbf{D}^{SS} \bullet \mathbf{V}^{SS} + c\mathbf{D}^{SL} \bullet \Pi^{LS} \\ & + c\mathbf{D}^{LS} \bullet \Pi^{SL} - 2mc^2 \mathbf{D}^{SS} \bullet \mathbf{S}^{SS} \\ & + \tfrac{1}{2}\{\mathbf{D}^{LL} \bullet \mathbf{I}^{LL,LL} \bullet \mathbf{D}^{LL} \\ & + \mathbf{D}^{LL} \bullet \mathbf{I}^{LL,SS} \bullet \mathbf{D}^{SS} + \mathbf{D}^{SS} \bullet \mathbf{I}^{SS,LL} \bullet \mathbf{D}^{LL} \\ & + \mathbf{D}^{LS} \bullet \mathbf{I}^{SL,LS} \bullet \mathbf{D}^{SL} + \mathbf{D}^{SL} \bullet \mathbf{I}^{LS,SL} \bullet \mathbf{D}^{LS} \\ & + \mathbf{D}^{SS} \bullet \mathbf{I}^{SS,SS} \bullet \mathbf{D}^{SS}\} \end{aligned} \tag{1}$$

with $\mathbf{D}$, $\mathbf{V}$, Π and $\mathbf{S}$ representing the density, potential energy, $\sigma \cdot p$ and overlap matrices, respectively. The two-electron integral matrix $\mathbf{I}$ is block diagonal in L and S

Table 1. Calculated bond distances (pm) using all Coulomb-type two-electron integrals, without the $\mathbf{I}^{SS,SS}$ class of integrals and with the SCC method

Molecule	Method	Full calculation	Without $\mathbf{I}^{SS,SS}$	With correction	Error after correction
Br_2	Hartree-Fock	227.7	227.7	227.7	−0.001
Br_2	CCSD(T)	231.5	231.4	231.5	−0.001
I_2	Hartree-Fock	268.2	267.6	268.2	−0.004
I_2	CCSD(T)	271.7	271.0	271.7	−0.003
At_2	Hartree-Fock	297.3	289.1	297.3	0.001
At_2	CCSD(T)	304.6	293.8	304.6	0.019

Table 2. Calculated harmonic frequencies (cm^{-1}) using all Coulomb-type two-electron integrals, without the $\mathbf{I}^{SS,SS}$ class of integrals and with the SCC method

Molecule	Method	Full calculation	Without $\mathbf{I}^{SS,SS}$	With correction	Error after correction
Br_2	Hartree-Fock	350.6	351.0	350.6	−0.000
Br_2	CCSD(T)	312.0	312.6	312.0	−0.002
I_2	Hartree-Fock	228.5	230.6	228.5	−0.010
I_2	CCSD(T)	205.8	208.4	205.8	−0.014
At_2	Hartree-Fock	131.4	148.9	131.4	−0.074
At_2	CCSD(T)	107.6	131.9	107.5	−0.112

$$\mathbf{I}^{VW,XY}_{ij,kl} = \iint \frac{\Psi_i^{V\dagger}(r_1)\Psi_j^{W}(r_1)\Psi_k^{X\dagger}(r_2)\Psi_l^{Y}(r_2)}{r_{12}}\delta_{VW}\delta_{XY}\,dr_1dr_2 - \iint \frac{\Psi_i^{V\dagger}(r_1)\Psi_l^{Y}(r_1)\Psi_k^{X\dagger}(r_2)\Psi_j^{W}(r_2)}{r_{12}}\delta_{VY}\delta_{XW}\,dr_1dr_2 \ . \tag{2}$$

The $\mathbf{I}^{SS,SS}$ class of integrals contributes only in the order of α^4 to the electronic energy. In Dirac-Hartree-Fock calculations the relative importance of these integrals to the *SS*-part of the Fock matrix is also of this order, because of the $2mc^2$ term that appears in this block. Omission of this class will therefore change the SCF wave function only slightly. So, we find that while the contribution of the $\mathbf{I}^{SS,SS}$ class of integrals is formally small, it does still influence calculated molecular properties of heavy elements significantly. The reason for this can be understood by explicitly calculating the population of the small components of the wave function. For the astatine atom this is 0.61 electron, which means that neglect of the $\mathbf{I}^{SS,SS}$ class leads to a significant underestimation of the electronic repulsion energy.

The molecular small component density of a molecule can, to a very good approximation, be regarded as a superposition of the atomic small component densities. Since the small component density arises mainly from core orbitals, it is highly localized and insensitive to the small variations induced in the valence region when the atoms form a bond. The missing contributions to the electronic energy upon neglecting $\mathbf{I}^{SS,SS}$-type integrals can be broken down into one-centre and multi-centre contributions. The one-centre contribution is dominant, but remains essentially the same as in the atom and does not influence the shape of the calculated potential energy surface. The multi-centre contribution does vary with distance, and it is this term that gives rise to the observed discrepancies. Since the overlap between the small component densities on different atoms is very small, one may in a first approximation neglect exchange contributions and approximate this term by only the Coulombic repulsion between the small component core densities. In general, this can be done by expanding the interaction in a multiple series. Here, I take the simplest approach and use only the first term of such an expansion, i.e. the charges, which are taken from a SCF calculation on the neutral atoms. The latter choice makes it possible to unambiguously define the charges on each atom, but it does neglect electron correlation effects and molecular polarization. Refinements of this simple procedure are, of course, possible and will be explored in subsequent papers. The current working procedure becomes then the addition of a distance dependent correction

$$\begin{aligned} \Delta E &= \sum_A \Delta E_A^{SS\ 1\text{-centre}} + \frac{1}{2}\sum_{A\neq B} E_{AB}^{SS-CR} \\ &= \sum_A \Delta E_A^{SS\ 1\text{-centre}} + \frac{1}{2}\sum_{A\neq B} \frac{q_A^S q_B^S}{R_{AB}}, \end{aligned} \tag{3}$$

to each point of the potential energy surface, calculated without the $\mathbf{I}^{SS,SS}$ integrals. In this formula q_A^S is the charge in the small component for atom A and $\Delta E_A^{SS\ 1\text{-centre}}$ is the difference between the energies for atom A, calculated with and without the $\mathbf{I}^{SS,SS}$ integrals. In the second term SS-CR stands for small-small interaction approximated by Coulombic repulsion. The simple Coulombic correction (SCC), formulated in this manner, is independent of the energy calculation and may be inserted when the potential energy surface is fitted and spectroscopic constants are calculated.

3 Results

I have applied the SCC method to the calculation of spectroscopic constants for the three heaviest halogen diatomic molecules. Details on the full four-component calculations are given in Ref. [6]. The present results are

Table 3. Total energies (E_h) using all Coulomb-type two-electron integrals, without the $\mathbf{I}^{SS,SS}$ class of integrals and with the SCC method. Bond lengths used were 4.37 a_o for Br_2, 5.12 a_o for I_2 and 5.76 a_o for At_2

Molecule	Method	Full calculation	Without $\mathbf{I}^{SS,SS}$	With correction	Error after correction
Br_2	Hartree-Fock	−5210.057137	−5210.418643	−5210.057128	0.000008
Br_2	CCSD(T)	−5210.418643	−5210.460350	−5210.418636	0.000007
I_2	Hartree-Fock	−14231.495103	−14231.938785	−14231.495079	0.000024
I_2	CCSD(T)	−14231.806256	−14232.249933	−14231.806237	0.000019
At_2	Hartree-Fock	−45819.284479	−45826.494043	−45819.284410	0.000069
At_2	CCSD(T)	−45819.546622	−45826.756126	−45819.546569	0.000052

Table 4. Calculated dissociation energies D_e (kcal mol^{-1}) using all Coulomb-type two-electron integrals, without the $\mathbf{I}^{SS,SS}$ class of integrals and with the SCC method

Molecule	Method	Full calculation	Without $\mathbf{I}^{SS,SS}$	With correction	Error after correction
Br_2	Hartree-Fock	15.7	16.4	15.7	−0.005
Br_2	CCSD(T)	39.2	39.9	39.2	−0.004
I_2	Hartree-Fock	9.2	13.6	9.2	−0.015
I_2	CCSD(T)	29.6	34.0	29.6	−0.012
At_2	Hartree-Fock	−8.2	33.9	−8.2	−0.044
At_2	CCSD(T)	14.6	55.9	14.6	−0.033

obtained with the same methods using triple zeta type basis sets, but with the $\mathbf{I}^{SS,SS}$ type integrals neglected throughout the calculations. The MOLFDIR code [7] was used. The atomic small component charges used were −0.0693603 e (bromine), −0.1894804 e (iodine) and −0.6096897 e (astatine) and were obtained from basis set Dirac-Hartree-Fock calculations on the $^2P_{3/2}$ ground states of the atoms. As can be seen from Tables 1–4, the correction procedure works remarkably well. Both at the Hartree-Fock and CCSD(T) level of theory the agreement between the full calculation and the approximated calculations is much better than the uncorrected results and satisfactory also on an absolute scale of precision. Given the frozen core approximation that is based on the atomic SCF results, one might expect that the CCSD(T) results will be somewhat worse than the SCF results. The current results do not show this trend, but the absolute errors are too small to make a reliable assessment of the differences. The size of the absolute errors is such that improvements of the method are not necessary for these molecules. It is to be expected that the errors will be larger when considering polar molecules, where the atomic charge distribution becomes more distorted. If necessary one may then use charges obtained from a molecular density analysis. From the correction it is also obvious why the results of previous uncorrected calculations without $\mathbf{I}^{SS,SS}$ integrals were so close to the full results. Most of these systems concerned hydrogen atoms bound to one heavy element. The small component charge for the hydrogen atom is −0.000013 e, so that the distant dependent term in the SCC-energy correction is only a few μHartrees.

The reduction in computation time resulting from the approximation can be judged by looking at the timings for the At_2 calculation. While a full calculation of a single point CCSD(T) energy for At_2 took 71 h of single processor time on a Cray J916, the approximate calculation took 27 h, an overall speed-up factor of 3. More important perhaps is that the disk requirements for the convential SCF algorithm were reduced from 5.2 GB to 1.5 GB.

4 Concluding remarks

The proposed simple a posteriori Coulombic approximation works very well for valence properties that depend directly on the total energy of the system. Generalization of the procedure for use in analytical calculations of derivatives with respect to internuclear distances is trivial. A more elaborate scheme that includes one-centre interactions explicitly in the molecular calculations is probably desirable for calculations of other energy derivatives like dipole polarizabilities and especially core-like properties such as NMR shieldings and spin-spin coupling parameters. On the other hand, one may envisage a similar use of the locality and atomic-like character of the small component density to approximate the $\mathbf{I}^{LL,SS}$-type integrals that contribute in an order of α^2 to the energy.

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References

1. Stanton RE, Havriliak S (1984) J Chem Phys 81: 1910
2. Lee YS (1986) Bull Korean Chem Soc 7: 480
3. Dyall KG (1992) Chem Phys Lett 196: 178
4. Pisani L, Clementi E (1994) J Comp Chem 15: 466
5. Saue T, Fægri K, Helgaker T, Gropen O (1997) Mol Phys 91: 937
6. Visscher L, Dyall KG (1996) J Chem Phys 104: 9040
7. Visscher L, Visser O, Aerts PJC, Merenga H, Nieuwpoort WC(1994) Comp Phys Comm 81: 120