Diagonal Born-Oppenheimer Correction Based on Spin-Free Relativistic Hamiltonians

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Methodologies beyond the Born-Oppenheimer (BO) approximation are nowadays important to explain high precision spectroscopic measurements. Our work is the first development and application of the diagonal BO correction (DBOC) based on spin-free relativistic Hamiltonians. We used the second and infinite-order Douglas-Kroll-Hess Hamiltonians at their spin-free levels. Our test calculations of noble atoms (He – Xe) show that the DBOC energy (EDBOC) is approximately proportional to atomic number Z . Hence the BO correction generally increases when a molecule contains heavier atoms. We also computed the adiabatic corrections to the barrier heights for linearization of H_2X molecules where $X = O, S, Se$, and Te , to discuss DBOC corrections for heavy elements.

Keywords: diagonal Born-Oppenheimer correction, relativistic effect, Douglas-Kroll-Hess, heavy element, spin free

1 Introduction

Electronic structure calculations in quantum chemistry are generally based on the Born-Oppenheimer approximation (BOA). The error generated by the BOA is negligibly small in most cases such as thermodynamics for chemical reactions or optimization of molecular geometries. However, the BOA breakdown is non-negligible compared to spectroscopic accuracy, where the BOA breakdown is observable by the current experimental techniques.

The first-order correction to BOA in perturbation theory is so-called diagonal Born-Oppenheimer correction (DBOC). DBOC is the expectation value of the nuclear kinetic-energy operators over the electronic wave function shown in Eq. (1).

$$E_{\text{DBOC}} = \sum_{A=1}^N -\frac{1}{2M_A} \langle \Psi(\mathbf{r}; \mathbf{R}) | \nabla_A^2 | \Psi(\mathbf{r}; \mathbf{R}) \rangle \quad (1)$$

Here, the summation runs over all Cartesian coordinates of a nucleus A in a molecule. Total number of nuclei is represented

as N . M_A is the corresponding nuclear mass in atomic units and ∇_A^2 is the second-derivative with respect to nuclear coordinate $\mathbf{R}_A$. $\Psi(\mathbf{r}; \mathbf{R})$ is the normalized electronic wave function depending on the electronic coordinates $\mathbf{r}$ and nuclear coordinates $\mathbf{R}$. DBOC was studied in 1986 by Handy et al. [1] at the Hartree-Fock (HF) level, and Lengsfeld et al. at the MCSCF level [2], using analytic derivative methods. More recently, electron correlation effects on DBOC have been considered at the configurational interaction (CI) level by Valeev and Sherrill [3] and the coupled-cluster (CC) level by Gauss et al. [4], using numerical and analytic differentiation, respectively. However all of these studies are based on the use of a non-relativistic Hamiltonian and are limited to molecules containing light atoms. Actually there is no knowledge as to whether the BOA breakdown is more or less significant in systems with heavy atoms.

Hence in this study, we have developed a program to evaluate the DBOC based on relativistic Hamiltonians at the restricted HF level. We have adopted the 2nd-order Douglas-Kroll-Hess methods (DKH2) [5,6] and infinite-order two-component

(IOTC) method [7–11] at their spin-free levels. (Since IOTC is conceptually equivalent to the infinite-order Douglas-Kroll-Hess method, we denote the IOTC method as DKH ∞ in this paper.) We do not consider the relativity of nuclei such as using the Klein-Gordon equation since the nuclear relativity must be smaller than electronic relativity. Hence Eq. (1) is valid in our relativistic case, although the first-order BO correction is different from Eq. (1) if we start from the Klein-Gordon equation for nuclei. We discuss how the DBOC terms change when molecular systems contain heavier atoms. We also discuss the relativistic effect on DBOC using as benchmarks the noble gas atoms (He – Xe) and water analogs (H₂X, X=O, S, Se, and Te).

2 Theory

E_{DBOC} in the restricted Hartree-Fock method is expressed in terms of molecular orbital integrals as follows.

$$\left\langle \psi_{\text{HF}} \left| \sum_{A=1}^N -\frac{1}{2M_A} \nabla_A^2 \right| \psi_{\text{HF}} \right\rangle = \sum_{A=1}^N -\frac{1}{2M_A} \left[2 \sum_i^n \langle \phi_i | \nabla_A^2 | \phi_i \rangle - 2 \sum_{i \neq j}^n \langle \phi_j | \nabla_A | \phi_i \rangle \langle \phi_i | \nabla_A | \phi_j \rangle \right] \quad (2)$$

Lower case i and j label the occupied orbitals in the restricted HF wave function with $2n$ electrons. The derivatives of a molecular orbital ϕ with respect to the nuclear coordinate ($R_A = X_A, Y_A$, or Z_A) are represented in Eq. (3) and Eq. (4).

$$\frac{\partial}{\partial R_A} \phi_i = \sum_k^m U_{ki}^{(1)} \phi_k + \phi_i^{(1)} \quad (3)$$

$$\frac{\partial^2}{\partial R_A^2} \phi_i = \sum_k^m U_{ki}^{(2)} \phi_k + 2 \sum_k^m U_{ki}^{(1)} \phi_k^{(1)} + \phi_i^{(2)} \quad (4)$$

Here, $\phi^{(1)}$ and $\phi^{(2)}$ are obtained by differentiation with respect to the nuclear coordinates in the basis-set functions. The index k runs over all the molecular orbitals. The total number of MOs is represented as m . $U^{(1)}$ and $U^{(2)}$ are the solution of coupled-perturbed Hartree-Fock (CPHF) equation [1]. The values of $U^{(2)}$ for DBOC are calculated from $U^{(1)}$ and $S^{(1)}$ as follows,

$$U_{ii}^{(2)} = -\frac{1}{2} S_{ii}^{(2)} - \sum_k^m \left[\left(U_{ik}^{(1)} \right)^2 - \left(S_{ik}^{(1)} \right)^2 \right] \quad (5)$$

so we need to solve only the CPHF for the first-derivatives [1].

Eq. (6) expresses a CPHF equation for the first derivative of a nuclear coordinate R . We omit the nuclear index A from R for simplicity.

$$\begin{aligned} & \left(\varepsilon_{\sigma}^{(0)} - \varepsilon_j^{(0)} \right) U_{\sigma j}^{(1)} \\ & + \sum_{k=1}^n \sum_{\tau=n+1}^m \left\{ \left(4[\sigma j | \tau k] - [\sigma k | \tau j] - [\sigma \tau | k j] \right) U_{\tau k}^{(1)} \right\} \\ & = \left(\varepsilon_j^{(0)} O_{\sigma j}^{(1)} - H_{\sigma j}^{(1)} \right) - \sum_{k=1}^n \left\{ \frac{\partial}{\partial R} \left(2[\sigma j | k k] - [\sigma k | k j] \right) \right\} \\ & - \sum_{k=1}^n \sum_{l=1}^n \left\{ O_{kl}^{(1)} \left(2[\sigma j | l k] - [\sigma k | l j] \right) \right\} \end{aligned} \quad (6)$$

Here, $O^{(1)}$ and $H^{(1)}$ are the first derivatives of overlap and one-electron-operator integrals. $[\sigma j | \tau k]$ etc., are the two-electron integrals at the molecular orbitals level, and $\varepsilon^{(0)}$ is an orbital energy. Note that the derivative with respect to R of the two-electron integrals only acts on the *nuclear coordinate in the basis set functions*. Indices j, k , and l run over all occupied molecular orbitals, while indices τ and σ run over virtual orbitals. From the non-linear equations represented in Eq. (6), $U^{(1)}$ are iteratively obtained. Readers may find more details in Ref [1,12].

Within the spin-free relativistic Hamiltonian, relativity affects only the term $H^{(1)}$ in Eq (6). Hence we used the numerical derivatives of the relativistic one-electron-operator integrals instead of the non-relativistic $H^{(1)}$ [13], with all other steps using analytic differentiation. We developed the programs to compute the relativistic DBOC in the GAMESS program package [14]. In our program we can also use the third-order DKH (DKH3) [15] in addition to DKH2 and DKH ∞ Hamiltonian at will. At present, we have a limitation to *spd* basis sets for our program, until *f*-type and higher integral derivatives become available.

3 Test Calculations and Discussions

3.1 E_{DBOC} in noble-gas atoms

Table 1 shows the E_{DBOC} of He, Ne, Ar, Kr, and Xe atoms at the non-relativistic, DKH2, and DKH ∞ levels. We used the Sapporo-DZP basis [16–18] for all elements. The three DBOC corrections with the different methods are almost the same for light atoms. However the deviation increases when the atom is heavier because relativity becomes important. For Xe, the relativistic correction to E_{DBOC} is around 7%. The differences between DKH2 and DKH ∞ are very small, below two decimal places for all the atoms.

Table 1. E_{DBOC} (cm^{-1}) of the noble-gas atoms at the non-relativistic, DKH2, and DKH ∞ levels.

Atoms	Non-rel.	DKH2	DKH ∞
He	85.91	85.91	85.91
Ne	683.87	680.77	680.77
Ar	1297.70	1280.84	1280.84
Kr	2873.62	2755.27	2755.27
Xe	4494.22	4158.61	4158.61

The E_{DBOC} obtained here approximately scales as Z , as shown in Figure 1. We can explain this observation as follows, though the scaling factor may not correspond to any simple physical concept. The form of E_{DBOC} in Eq. (2) has some resemblance to the form of the kinetic energies of electrons (K_e) at HF shown in Eq (7).

$$K_e = \sum_{i=1}^n 2 \langle \varphi_i | -\frac{1}{2} \nabla^2 | \varphi_i \rangle \quad (7)$$

Especially in atomic cases, we only consider the basis set functions belonging to the one-center of the nucleus. Therefore, the derivatives with respect to the electronic coordinates can be easily related to derivatives with respect to the nuclear coordinate. That means if we ignore the second terms in Eq. (2) and the terms containing U in Eq. (3) and (4), Eq. (2) and Eq. (7) only differ in the scaling factor of $1/M$. Because the electronic kinetic energy can be related to the total electronic energy if we assume the Virial Theorem, the total energy approximately scales as Z^2 , according to Hydrogen-like atomic energies. The factor of $1/M$ roughly scales as $1/Z$, and therefore, E_{DBOC} scales as $Z^2 \times (1/Z) = Z$.

3.2 E_{DBOC} in H_2X molecules

Table 2 shows another example of E_{DBOC} in H_2X molecules ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{and Te}$). We optimized their bent and linear molecular structures under C_{2v} and $\text{D}_{\infty h}$ symmetry constraint using

Figure 1. E_{DBOC} (cm^{-1}) vs atomic number Z in the noble-gas atoms at the DKH ∞ levels.

a non-relativistic Hamiltonian and obtained E_{DBOC} . We used the same non-relativistic molecular structures in Table 3 for the E_{DBOC} calculations to simplify the comparison with DKH ∞ level E_{DBOC} . The E_{DBOC} difference between the C_{2v} and $\text{D}_{\infty h}$ symmetries (ΔE_{DBOC}) corresponds to an adiabatic correction to the barrier height to linearization of H_2X molecules. Similar to the atomic cases, the DBOC corrections to these barrier height energies increase when the system contains heavier elements. Only the ΔE_{DBOC} in H_2O shows negative value. This is caused by taking subtractions of two DBOC energies (C_{2v} and $\text{D}_{\infty h}$) which are independently scaled to Z with different scaling factors. In H_2Te , the relativistic correction to ΔE_{DBOC} is about 20%. Barrier heights at the Born-Oppenheimer approximation (BOA) are shown in Table 4 as ΔE . Note that the BOA barrier heights do not scale according to atomic number Z . In fact, H_2S , H_2Se , and H_2Te have similar linearity barriers noticeably larger than for H_2O . This is because the bend angle of the optimized H_2O molecule is 104° whereas those of the other molecules are around 93° as shown in Table 3. That means the bent H_2O molecule is more close to the linear H_2O molecule and its barrier

Table 2. Absolute values of E_{DBOC} in C_{2v} and $\text{D}_{\infty h}$ H_2X molecules ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{and Te}$), and DBOC (i.e. adiabatic corrections) for barrier to linearity of these molecules, ΔE_{DBOC} in cm^{-1} .

DBOC	Non-rel.			DKH ∞		
	C_{2v}	$\text{D}_{\infty h}$	ΔE_{DBOC}	C_{2v}	$\text{D}_{\infty h}$	ΔE_{DBOC}
H_2O	598.1	583.7	-14.4	596.6	582.2	-14.4
H_2S	1344.0	1379.3	35.3	1330.7	1367.4	36.7
H_2Se	2759.3	2822.8	63.5	2658.3	2730.6	72.3
H_2Te	4304.9	4421.0	116.1	4005.8	4149.2	143.4

Table 3. Optimized geometry of H₂X molecules (X = O, S, Se, and Te) in C_{2v} and D_{∞h} structures.

	C _{2v}		D _{∞h}
	R _{HX} (Å)	θ _{HXH} (°)	R _{HX} (Å)
H ₂ O	0.945	104.7	0.923
H ₂ S	1.338	93.9	1.320
H ₂ Se	1.462	93.0	1.427
H ₂ Te	1.662	92.5	1.614

Table 4. Barrier heights for linearity (ΔE) of H₂X molecules (X = O, S, Se, and Te) in cm⁻¹ within the Born-Oppenheimer approximation.

ΔE	Non-rel.	DKH _∞
H ₂ O	12211.8	12258.3
H ₂ S	28666.0	28822.4
H ₂ Se	30178.4	30546.9
H ₂ Te	30106.9	30658.2

becomes lower than the cases of the other molecules. Though there is some exception for H₂O, the barriers to linearity are the same size for all H₂X molecules while the DBOC energy correction increases *systematically* with Z. Hence inclusion of DBOC may be more important in heavy atom systems.

4 Conclusions

We have developed the theory and program to compute E_{DBOC} within the spin-free DKH2, DKH3, and DKH_∞ methods using the GAMESS program. Numerical derivatives of the relativistic one-electron integrals [14] are used during the otherwise fully analytic computation [1] of DBOC by CPHF. The test calculations of both atoms and molecules show the DBOC energy corrections become larger when the system contains heavier atoms, and are approximately proportional to the atomic number Z. The relativistic corrections to E_{DBOC} grow to about 7% for rare gas atoms and about 20% for H₂X linearity barriers, when Z is around 50. In particular, not only is DBOC itself apparently larger in heavy molecules, its accurate evaluation requires inclusion of scalar relativistic corrections such as DKH_∞. Since the DBOC has been discussed only in light elements so far [1,3,4], further investigation with general molecules containing heavy elements will be important. We are currently working on the extension of basis set derivatives to g-type functions to be able to calculate much heavier elements.

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