Effects of the Magnetic Part of the Breit Term on Bonding : Model Calculations with Small Diatomic Molecules

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Model calculations for small molecules Li_2, F_2, LiF and BF have been performed at the Dirac-Fock level of theory using Dirac-Coulomb and Dirac-Coulomb-Magnetic Hamiltonians with various basis sets. In order to understand what may happen when the relativity becomes significant, the value of c, speed of light, is varied from the true value of 137.036 a.u. to 10^5 (nonrelativistic case) and also to 50 and 20 a.u. (exaggerated relativistic cases). Qualitative trends are discussed with special emphasis on the effect of the magnetic part of the Breit interaction term. The known relativistic effects on bonding such as the bond length contraction or expansion are demonstrated in this model study. Total energy, π-orbital splitting, bond length, bond dissociation energy and dipole moment are calculated, and shown to be modified in a uniform direction by the effect of the magnetic term. Inclusion of the magnetic term raises the total energy, increases the bond length, reduces the π-orbital splitting, increases the bond dissociation energy, and mitigates the changes in dipole moment caused by the Dirac term.

Keywords : Dirac-Fock calculation, Relativistic effects, Breit interactions, Dirac-Coulomb-Magnetic Hamiltonian.

Introduction

The Dirac-Fock (DF) theory is a relativistic Hartree-Fock theory, and derived by replacing the kinetic operator in the Hamiltonian for a many electron system with the Dirac operator. The resulting four-component coupled equation has been a challenge to many quantum physicists and chemists.[1-3] For atomic systems, many attempts have been made to solve the equation with either the numerical method[4-6] or the basis expansion method.[7] The basis set expansion method has also been applied to molecules, and is becoming a standard method with many available results.[8-10]

When the Coulomb potential is used for electron interactions in the DF theory, the Hamiltonian, which is usually referred to as the Dirac-Coulomb (DC) Hamiltonian, does not contain any relativistic interactions between electrons. The first correction to the DC Hamiltonian is the Breit term, which is the largest term next to the Coulombic interaction in the quantum electrodynamics,[11,12] and its zero-frequency form is written as follows.

$$
\begin{aligned}
H_B &= H_M + H_R \\
&= -\sum_{i<j} \frac{\alpha_i \cdot \alpha_j}{r_{ij}} + \sum_{i<j} \frac{[(\alpha_i \cdot \nabla_i)(\alpha_i \cdot \nabla_i) r_{ij}]}{2}
\end{aligned}
\tag{1}
$$

The Breit term consists of the magnetic part (which is also called the Gaunt interaction term[13]) and the retardation part. The former is the dominant part of the whole Breit term and can be incorporated with relative ease into the DC Hamiltonian, and the resulting Hamiltonian may be called the Dirac-Coulomb-Magnetic (DCM) Hamiltonian. The use of the DC and the DCM Hamiltonians in the DF method leads to relativistic self-consistent-field (RSCF) methods, which we refer to DC-RSCF and DCM-RSCF, respectively. Our previous reports on relativistic calculations for diatomic hydrides demonstrate the reliability of this RSCF method.[14-17] In addition to our RSCF method, which is based upon Slater type orbitals (STOs), several RSCF programs using Gaussian type orbitals (GTOs) also have been reported.[18-20] Especially, Visscher et al. have been develo-ped the MOLFDIR package[18] which uses both the DC and DCM Hamiltonians in DF and post-DF methods.

Although many reviews about theoretical approach[21,22] and calculated numerical results[23] are available for the relativistic effects on bonding, there are few papers conducting a detailed analysis on the effects of the magnetic part of the Breit term. The magnitude of the effects by the magnetic part is considered negligible,[24-26] but the trend of it has rarely been discussed quantitatively. In this work, we examine the effects of the magnetic part on bonding by calculating electronic structures of Li_2, F_2, LiF, and BF at the DF level using both STO and GTO basis sets. Since the true relativistic effects on the above molecules are small, we perform calculations on models for which relativistic effects are artificially amplified by treating the speed of light as a variable parameter. We will follow changes caused by the magnetic part in the artificially intensified relativistic environments.

The sign of the Breit term differs from that of Dirac operator, and the effect of the Breit term will be the reverse of those of the Dirac operator only. Because the Breit term is of the order of $(v/c)^2$ compared to the nonrelativistic interaction term, the magnetic part of the Breit term will increase as the value of c decrease or the average velocity of an electron increase. As will be discussed later, this viewpoint could be useful in rationalizing the observed effects of the Breit term on bonding.

In the following sections, calculations on small diatomic molecules, Li_2, F_2, LiF, and BF are described, and data obtained from the calculations are analyzed to establish a few trends.

Computational Details

Two RSCF programs are employed as the main tools of this study. The one developed by us uses the Slater-type basis functions while the other, whose original name is MFDSCF in MOLFDIR, employs the Gaussian-type basis.

The double zeta Slater-type orbital (STO-DZ) basis sets for the large-component space are taken from nonrelativistic atomic SCF calculations of Clementi and Roetti.[27] We added two 2p functions with the same exponent as 2s to the basis set for Li while the basis sets for B and F were used as they are. The STO-DZ* basis sets are made by augmenting a 2p-type STF with exponent of two thirds of the smallest 2p exponent in the original STO-DZ basis set. As for the Gaussian basis sets for the large-component space, we used the standard Gaussian basis sets 6-31G, 6-311G, and 6-311G* for all the atoms of interest.[28,29] All primitive GTOs in the sets are used without contraction. The basis sets in the present relativistic calculations satisfy the kinetic balance condition.[30,31,32] Though the 'kinetic balance' is not an exact relation for the cases with very small value of c, unconstrained variation of the expansion coefficients will provide enough flexibility for the following qualitative analyses.

We also applied an auxiliary program to the systems of interest to guarantee the reliability of our calculations. The Hartree-Fock program in the ALCHEMY package[33] was used to assess the nonrelativistic limit obtained by the RSCF programs with STO bases. The nonrelativistic program ALCHEMY was used only with the large components of the basis set used in RSCF and yield the same results as RSCF at the nonrelativistic limit, *i.e.* with 10^5 a.u.

The equilibrium internuclear distances of small molecules Li_2, F_2, LiF, and BF are determined by calculating total energies with the RSCF programs in conjunction with different bases. The procedure was repeated by changing the value of c to 50 and 20 a.u. to make the exaggerated relativistic environments and to 10^5 a.u. to reproduce the nonrelativistic limit. We observed changes in the equilibrium bond length and the total energy of each molecule as c decreases. The effects of the magnetic part of the Breit term on results are appreciated while the geometries are optimized with the DC-RSCF or DCM-RSCF methods. In addition to that, LiF and BF are studied in detail to elucidate how orbitals and spin-orbit interactions change in the intensified relativistic environments, and to estimate magnetic corrections to orbital energies, spin-orbit interactions, geometries, and dipole moments.

For LiF and BF, we also used several Gaussian basis sets to calculate the equilibrium distances, and compared the data with those with STO basis. We tried to estimate and thus eliminate the basis set truncation error from the effect of the magnetic part.

Results and Discussion

First, we consider the homonuclear cases, Li_2 and F_2. Our model calculations for both molecules, given in Table 1 and Table 2, show a trend as the value of c is varied in DC-RSCF and DCM-RSCF methods with Slater-type basis functions.

For the DC-RSCF results in Table 1, the equilibrium internuclear distance of Li_2 is shortened as c decreases, indicating that noticeable relativistic effects are artificially induced. The variation in equilibrium distance of Li_2 with the decrease of c can be attributed to the contractions of s atomic orbitals participating in the bond. The same rule does not hold for the F_2 case, in which there are two π-orbital splittings, $\Delta\pi$ and $\Delta\pi^*$. The results depend on the basis sets. With the STO-DZ basis set, the same phenomenon, *i.e.*, the bond contraction, seems to occurs with one exception at

Table 1. The equilibrium distances (in a.u.)[a] of Li_2 and F_2 with the STO basis set

	Basis	STO-DZ		STO-DZ	
	value of c	DC-	DCM-	DC-	DCM-
Li_2	10^5	5.2609	5.2609	5.2556	5.2556
	137.0360	5.2605	5.2607	5.2552	5.2554
	50	5.2579	5.2592	5.2525	5.2538
	20	5.2421	5.2500	5.2365	5.2445
F_2	10^5	2.6716	2.6716	2.6344	2.6344
	137.0360	2.6713	2.6718	2.6346	2.6351
	50	2.6710	2.6742	2.6374	2.6405
	20	2.7044	2.7164	2.7033	2.7130

[a]The experimental values are 5.0510 and 2.6682 a.u., respectively[38].

Table 2. The valence orbital energies of F_2 calculated with the STO-DZ basis set at 2.7000 a.u. near the experimental equilibrium distance as the value of c is varied. All values are in atomic units.

value of c	20	50	137.0360	10^5
DC-RSCF				
E_{total}	-207.54091	-200.10948	-198.91081	-198.72762
$\varepsilon(1\pi_{1/2})$	-0.82007	-0.81546	-0.81577	-0.81585
$\varepsilon(2\pi_{3/2})$	-0.73041	-0.80274	-0.81412	-0.81585
$\varepsilon(5\sigma)$	-0.77571	-0.73688	-0.73913	-0.73998
$\varepsilon(3\pi^*_{1/2})$	-0.59954	-0.67735	-0.68053	-0.68048
$\varepsilon(4\pi^*_{3/2})$	-0.58911	-0.66653	-0.67865	-0.68048
DCM-				
E_{total}	-206.38371	-199.92948	-198.88701	-198.72762
$\varepsilon(1\pi_{1/2})$	-0.81093	-0.81423	-0.81561	-0.81585
$\varepsilon(2\pi_{3/2})$	-0.73097	-0.80266	-0.81410	-0.81585
$\varepsilon(5\sigma)$	-0.76201	-0.73594	-0.73910	-0.73998
$\varepsilon(3\pi^*_{1/2})$	-0.60370	-0.67655	-0.68033	-0.68048
$\varepsilon(4\pi^*_{3/2})$	-0.58827	-0.66620	-0.67859	-0.68048

c=20. With the STO-DZ* basis set, however, the equilibrium distance even at the true value of c is longer than the nonrelativistic one, and the bond length increases further as the value of c decreases more. Other calculations with a larger basis set having a very large exponent for an 1s type STF, or with a Gaussian basis set, support the same conclusion that the bond expands for F_2. The phenomenon has also been observed for I_2 and At_2 by Visscher *et al.*,[22] and our results show that the effect can be amplified by reducing the value of c in the present work. The spin-orbit splitting for the molecular orbitals overcomes the mass-velocity effects and make the equilibrium distance longer than that at c=10^5. Thus, this case shows that, for molecules influenced by spin-orbit couplings, the basis set large enough to describe the splitting properly is indispensable.

In contrast to the bidirectional effect on the bond length, *i.e.*, the contraction or expansion by the DC method, the inclusion of the magnetic part of the Breit term by the DCM method consistently shows bond-lengthening effect compared with the results by the DC method, at all tested values of c. The effect becomes larger for the smaller c. The magnitude of the magnetic effects is not very sensitive to the size of basis set.

In an effort to understand the trend in Table 1, we examine, in Table 2, valence orbital energies of F_2 calculated with the STO-DZ basis set at R=2.700 a.u, near the experimental equilibrium distance. At the extreme case of c=20, the first $\Delta\pi$ of the two is so great that the destabilized $2\pi_{3/2}$ orbital goes over $5\sigma_{1/2}$ and greatly reduce the bonding, which results in the bond expansion shown in Table 1. The above phenomena in these model calculations can be applied to the explanation of the bond length expansions of real examples.[34] Later, we will see this behavior of again in the heteronuclear cases LiF and BF where the orbitals are not of bonding character but of nonbonding character. All the splittings can be ascribed to the p atomic orbital splitting of F.

DCM-RSCF does not change the trends in $\Delta\pi$. The inclusion of the magnetic part of the Breit term, however, raises most orbital energies including those of core orbitals not shown in Table 2.

In the heteronuclear diatomic molecules LiF and BF, the orbital characters of the molecules are analyzed in the artificially intensified relativistic environment. The orbital behaviors at the equilibrium internuclear distance with the various values of c are listed in Tables 3 and 4. The total energy and the orbital energies at a given value of c from DC-RSCF and DCM-RSCF calculations are shown in the Tables. As a reference nonrelativistic limit, provided are data labeled as NRSCF which are obtained with the ALCHEMY program [33] with the same basis as the large component basis set in the RSCF program. It is also noted that both DC-RSCF and DCM-RSCF give the same results at c=10^5. The total energy is lowered with the decrease of c but the magnetic term lifts it as in the case of homonuclear molecules. Once the relativity is intensified by the reduced value of c, core orbital energies are lowered while valence orbital energies are raised. The amounts of changes in valence orbital energies are just less than one tenth of those in core orbital energies, leading to the lowering of the total energy. In DC-RSCF, 1σ, 2σ, and 3σ orbitals originate from 1s and 2s orbitals of F and 1s orbital of Li or B, respectively. The behaviors of orbital energies suggest that the inner shells of the atoms are becoming more compact when the relativity is intensified. There are three valence orbitals in LiF. One of them $4\sigma_{2/1}$ is the bonding orbital and the other two π's are of nonbonding character. In BF, besides the three orbitals, there is an antibonding orbital $5\pi_{2/1}$. The DCM-RSCF method yields the similar but less obvious orbital behavior compared to DC-RSCF. The general feature result-

Table 3. The orbital energies for LiF calculated with the STO-DZ* basis set as the value of c is varied at R = 2.9554 *a.u.* All values are in atomic units

Value of c	20	50	137.0360	10^5	
DC-RSCF					NRSCF
E_{total}	-111.39329	-107.66966	-107.06819	-106.97624	-106.97624
$\varepsilon(1\sigma)$	-27.44120	-26.31950	-26.13395	-26.10565	-26.10616
$\varepsilon(2\sigma)$	-2.45942	-2.44972	-2.44807	-2.44781	-2.44781
$\varepsilon(3\sigma)$	-1.56174	-1.40294	-1.37977	-1.37635	-1.37654
$\varepsilon(4\sigma)$	-0.55198	-0.49612	-0.49380	-0.49406	-0.49424
$\varepsilon(1\pi_{1/2})$	-0.43354	-0.47124	-0.47133	-0.47086	-0.47102
$\varepsilon(2\pi_{3/2})$	-0.41564	-0.46176	-0.46960	-0.47086	-0.47102
DCM-RSCF					
E_{total}	-110.80155	-107.57737	-107.05598	-106.97624	
$\varepsilon(1\sigma)$	-27.04985	-26.25934	-26.12600	-26.10565	
$\varepsilon(2\sigma)$	-2.44910	-2.44807	-2.44785	-2.44781	
$\varepsilon(3\sigma)$	-1.55323	-1.40211	-1.37967	-1.37635	
$\varepsilon(4\sigma)$	-0.53987	-0.49489	-0.49372	-0.49406	
$\varepsilon(1\pi_{1/2})$	-0.43337	-0.47080	-0.47119	-0.47086	
$\varepsilon(2\pi_{3/2})$	-0.41574	-0.46187	-0.46961	-0.47086	

Table 4. The orbital energies for BF calculated with the STO-DZ* as the value of c is varied at R = 2.4463 a.u. All values are in atomic units.

Value of c	20	50	137.0360	10^5	
DC-RSCF					NRSCF
E_{total}	-128.84965	-124.85443	-124.20898	-124.11030	-124.11029
ε (1σ)	-27.69919	-26.58469	-26.40107	-26.37292	-26.37265
ε (2σ)	-7.84439	-7.76549	-7.75221	-7.75017	-7.75020
ε (3σ)	-1.86455	-1.72199	-1.70166	-1.69862	-1.69852
ε (4σ)	-0.85460	-0.83166	-0.83204	-0.83221	-0.83212
ε ($1\pi_{1/2}$)	-0.72861	-0.73574	-0.73376	-0.73338	-0.73329
ε ($2\pi_{3/2}$)	-0.66985	-0.72291	-0.73198	-0.73338	-0.73329
ε (5σ)	-0.42279	-0.42144	-0.42099	-0.42091	-0.42092
DCM-RSCF					
E_{total}	-128.19717	-124.75261	-124.19551	-124.11030	
ε (1σ)	-27.30835	-26.52444	-26.39312	-26.37292	
ε (2σ)	-7.78673	-7.75633	-7.75100	-7.75017	
ε (3σ)	-1.85694	-1.72121	-1.70157	-1.69862	
ε (4σ)	-0.84617	-0.83108	-0.83198	-0.83221	
ε ($1\pi_{1/2}$)	-0.72572	-0.73469	-0.73361	-0.73338	
ε ($2\pi_{3/2}$)	-0.67022	-0.72299	-0.73199	-0.73338	
ε (5σ)	-0.42082	-0.42109	-0.42094	-0.42091	

ing from the inclusion of the magnetic term is again to raise most orbital energies.

The π-orbital splittings, $\Delta\pi$, of LiF and BF around the equilibrium bond length are calculated with the variation of the internuclear distance. We compare $\Delta\pi$ at the true value of c with that at reduced values of c in Table 5. As the internuclear distance becomes shorter, $\Delta\pi$ tends to be smaller. The values in DCM-RSCF are reduced from those in DC-RSCF, from which we can interpret the magnetic term in a role of reducing π orbital splittings. As mentioned earlier, the effect of the Breit term will increase as the order of $(v/c)^2$ and the average value of v of an electron is larger for inner orbitals than for outer orbitals. The orbital energy destabilization for $\pi_{2/1}$ orbitals, therefore, is larger than that for $\pi_{3/2}$ orbitals, resulting in the reduction of π-orbital splitting. When we set c=20 in RSCF, expecting immense relativistic effects, splittings $\Delta\pi$, of course, become larger with the same tendency mentioned. Because the π-orbitals in LiF and BF have nonbonding character, $\Delta\pi$ can be directly compared with the spin-orbit splitting of F atom, 0.00184 a.u.[35]

Table 6 summarizes bond lengths with various basis sets. Data obtained from calculations with the STO-DZ basis set for heteronuclear diatomic molecules exhibit the same trends as in homonuclear cases. The equilibrium distance shortens as c is reduced and the magnetic part of the Breit term displays bond-lengthening effects. Calculations with the STO-DZ* basis set give the same result but with one exception for LiF, the bond length is longer at c=20 than at c=50. This bond expansion comes from the additional diffuse 2p functions added to the STO-DZ basis set. The π bonds gain some bonding character and their splitting resembles the π bonds of F_2. Although this phenomenon is somewhat factitious, the role of the magnetic term is still the same in this case.

Table 5. The spin-orbit splitting $\Delta\pi$ for the π orbitals[a] of LiF and BF calculated with the STO-DZ* basis set. All values are in atomic units.

		RSCF(137.0360)		RSCF(c = 20)	
	R	DC-	DCM-	DC-	DCM-
LiF	2.50	0.00169	0.00154	0.01596	0.01532
	2.60	0.00171	0.00155	0.01761	0.01704
	2.70	0.00172	0.00156	0.01842	0.01793
	2.80	0.00173	0.00157	0.01857	0.01818
BF	2.20	0.00174	0.00157	0.05645	0.05310
	2.30	0.00176	0.00159	0.05769	0.05434
	2.40	0.00178	0.00161	0.05849	0.05521
	2.50	0.00179	0.00163	0.05898	0.05577

[a] Spin-orbit splitting between $P_{3/2}$ and $P_{1/2}$ state of F atom is 0.00184 a.u. [35]

With the standard Gaussian basis sets, we reproduce the trends with STO. All basis sets produce bond length contraction as the value of c is decreased and the introduction of the magnetic term still expands the bond length. As the value of c is decreased, the bond length expansion by the magnetic term sometimes overcome the bond length contraction by the relativistic effects without it, which results in overall bond length expansion. An interesting point is that the amount of the bond lengthening by the magnetic term is not so dependent on the size of the basis set. Even with a small basis set, the magnetic correction to the internuclear distance is close to that with a large basis set. The relativistic bond length contraction for LiF and BF can be partially attributed to the contraction of 2s and $2p_{1/2}$ overcoming the expansion of $2p_{3/2}$, but other details of the bonding could be the major factor in determining the actual bond length.

Table 6. The equilibrium distances[a] (in a.u.) of LiF and BF.

		STO-DZ		STO-DZ*		6-31G		6-311G		6-311G*	
	Value of c	DC-	DCM-	DC-	DCM-	DC-	DCM-	DC-	DCM-	DC-	DCM-
LiF	100000	2.8661	2.8661	2.9553	2.9553	2.9203	2.9203	2.9791	2.9791	2.9628	2.9628
	137.036	2.8654	2.8657	2.9551	2.9554	2.9198	2.9201	2.9787	2.9791	2.9624	2.9628
	50	2.8606	2.8631	2.9542	2.9565	2.9169	2.9193	2.9763	2.9791	2.9598	2.9627
	20	2.8352	2.8504	2.9621	2.9751	2.9057	2.9198	2.9727	2.9891	2.9548	2.9713
BF	100000	2.4467	2.4467	2.4462	2.4462	2.4347	2.4347	2.4148	2.4148	2.3646	2.3646
	137.036	2.4461	2.4465	2.4459	2.4463	2.4342	2.4346	2.4143	2.4148	2.3642	2.3645
	50	2.4418	2.4449	2.4442	2.4472	2.4314	2.4345	2.4119	2.4150	2.3611	2.3640
	20	2.4178	2.4358	2.4391	2.4563	2.4228	2.4409	2.4073	2.4256	2.3504	2.3673

[a]The experimental values are 2.9553 and 2.3860 a.u. [38] for LiF and BF, respectively.

It is already mentioned that the 'kinetic balance condition' in basis sets is no longer a sufficient condition for a small value of c like to c=20. Error due to this approximation does not influence our result since small component basis sets are not contracted.

In our calculations, small molecules of homonuclear or heteronuclear, exhibit quite small relativistic effects, as can be estimated as the difference between data with $c=10^5$ to those with c=137.0360 a.u. They show negligibly small bond contractions with basis sets of moderate sizes. Bond length contractions in heavy atom containing molecules are well known,[23] and sometimes related to the orbital contraction.[36,37] In the same vein, one can contrive the bond expansion also shown for some molecules. Although our calculations are limited to small model molecules and the relativity is artificially increased to mimic systems having heavy atoms, it is clear that other relativistic effects like spin-orbit couplings and the Breit interactions are reasonably represented in this model study.

We also calculated two other properties for the heteronuclear molecules. Bond dissociation energies of LiF and BF at the equilibrium distances calculated with the STO-DZ* basis set are displayed in Table 7. In both molecules, the bond dissociation energies decrease as the relativity increases. The spin-orbit lowering of the open-shell atomic state are larger than that for the closed-shell molecules because of the spin-orbit splitting of the ^2P states. Once the magnetic part of the Breit term is included, bond energies are consistently increased. The absolute amount of the effect by the magnetic term and its relative values to the whole bond energies are growing as the value of c decreases. The energy destabilization by the magnetic part is larger for the free atoms than the molecules. In other words, spin-orbit stabilization of open-shell atoms is reduced by the magnetic term.

Table 7. The bond dissociation energies (in a.u.) of LiF and BF calculated with the STO-DZ* basis set

	Value of c	DC	DCM
LiF	10^5	0.141624	0.141624
	137.036	0.140506	0.140514
	50	0.133263	0.133319
	20	0.090980	0.091246
BF	10^5	0.180475	0.180475
	137.036	0.179387	0.179393
	50	0.172383	0.172424
	20	0.133509	0.133579

Table 8. The dipole moments of LiF and BF at the bond length of R=2.9554 a.u. for LiF and R=2.4463 a.u. for BF (the left part) and at the equilibrium bond length of each method (the right part)

	Value of c	At the selected bond length		At each equilibrium bond length	
		DC-	DCM-	DC-	DCM-
LiF	10^5	6.77141	6.77141	6.77118	6.77118
	137.036	6.77034	6.76983	6.76963	6.76983
	50	6.76230	6.75867	6.75947	6.76126
	20	6.65726	6.64027	6.67250	6.68499
BF	10^5	-0.21473	-0.21473	-0.21503	-0.21503
	137.036	-0.21376	-0.21477	-0.21496	-0.21477
	50	-0.20852	-0.21587	-0.21477	-0.21321
	20	-0.21803	-0.25727	-0.23857	-0.22827

Dipole moments for LiF and BF are calculated with the STO-DZ* basis set. Table 8 shows the changes of dipole moments at the fixed nuclear distances as well as those at the equilibrium bond distance of each method. The left part of Table 8 is the results along the change of c at R=2.9554 and 2.4463 for LiF and BF, respectively, the equilibrium bond lengths of LiF and BF by the DCM-RSCF with the STO-DZ* basis set at c=137.036. The right part of the table, on the other hand, is the results at the equilibrium bond length of each method. The left part shows that the values of the dipole moment decrease (the sign included) as the value of c decreases. One exception is at c=20 in BF. It is noteworthy that the magnetic term decreases the values of the dipole moments (the sign included) consistently at all values of c, which means that the charge of F is reduced, losing electron densities, at the fixed internuclear distance due to the magnetic term. The right part of the table reveals another trend in dipole moment. The dipole moment has a larger value when the magnetic term is included. Since geometries are changed, the results imply that geometric effects are in opposing or mitigating the charge shift effects of the magnetic term.

Concluding Remarks

Small molecules, Li_2, F_2, LiF and BF, have been calculated by the RSCF method. They hardly exhibit any relativistic effects when c=136.0360 a.u., the true value of the speed of light. By decreasing the value of c and thus intensifying relativistic effects artificially, we found that molecular properties such as bond length, dissociation energy, and dipole moment could be changed. Although this model calculation is just phenomenological without further analysis on molecules containing real heavy elements, the qualitative aspects of relativistic effects on bonding in this study are well in line with several theoretical analyses[21,22] and actual numerical calculations of heavy systems.[23] The present predictions about the effects of the magnetic part of the Breit interactions are reasonable and expected to be applicable to heavier systems. The effects of the magnetic part of the Breit term are summarized as follows. The magnetic term shows bond-lengthening effects, which is seemingly insensitive to the size of basis set. Other molecular properties are also changed by the magnetic part, among which are reduction of the spin-orbit splitting, increase in bond dissociation energy, and decrease in dipole moment. It is concluded that the magnetic term leads to changes in molecular properties in a direction mitigating the changes induced by the Dirac-Coulomb Hamiltonian.

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