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Is the Lamb shift chemically significant?

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Abstract

The contribution of the Lamb shift to the atomization energies of some prototype molecules, BF_3 , AlF_3 , and GaF_3 is estimated by a perturbation procedure. It is found to be in the range 3–5% of the one-electron scalar relativistic contribution to the atomization energy. The maximum absolute value is 0.2 kcal/mol for GaF_3 . These sample calculations indicate that the Lamb shift is probably small enough to be neglected for energetics of molecules containing light atoms if the target accuracy is 1 kcal/mol, but for higher accuracy calculations and for molecules containing heavy elements it must be considered. © 2001 Elsevier Science B.V. All rights reserved.

In the search for chemical accuracy in the quantum chemical calculation of molecular energetics, it has long been recognized that the principal contribution, and the one which is the hardest to evaluate, is that of electron correlation. This contribution requires large basis sets and sophisticated correlation methods, and even then an extrapolation procedure [1,2] is usually necessary to obtain a result which is accurate to better than 1 kcal/mol – the much-touted ‘chemical accuracy’ target. For those systems that are well described by

a single reference configuration, there has been progress in reducing the errors towards the 0.1 kcal/mol range [3,4].

It has often been assumed that, for constituent atoms from the first and second rows of the periodic table, the electron correlation contribution is the only contribution important for chemical accuracy. This assumption has been shown to be false for a number of systems, where the scalar one-electron relativistic contribution to the atomization energy is nearly 1 kcal/mol [5,6]. The scalar relativistic energy grows in the valence region at least as Z^2 [7], and for heavy elements can be tens of kcal/mol. It is also well recognized that the spin–orbit splitting of the atomic energy levels can make a significant contribution to the energetics of molecular processes, such as atomization energies. Even if the contribution of the splitting is smaller

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per atom than the desired accuracy, the total effect can be significant since all atomic spin–orbit contributions to the atomization energy have the same sign. While many atomization energies involve closed-shell molecules that have no molecular spin–orbit effect, the calculation of individual bond energies often involve open-shell systems where molecular spin–orbit effects can make an important contribution.

If the lowest order one-electron scalar relativistic contribution is large enough to be chemically significant, there may be other contributions which are also large enough. One obvious choice is the two-electron scalar relativistic contribution. The principal scalar two-electron relativistic term to be included is the two-electron Darwin term, which behaves as $\delta(r_{ij})$ but has no scaling factor involving Z , and has been found to be mostly small [8], though it is not necessarily negligible. Two-electron scalar relativistic effects are approximately incorporated in calculations that use the Douglas–Kroll–Hess method [9,10].

At the next order in the fine structure constant α is the Lamb shift. It has been found for the valence shells of atoms to be roughly the same size as the Breit interaction [11] which gives rise to the two-electron Darwin interaction. For hydrogenic light atoms it can be estimated by perturbation theory [12]. The operator used in the perturbation expansion is $\delta(r)$, which is the same as in the Darwin operator, but there is a scaling factor which depends on the principal quantum number n . It was recently proposed [13] that for molecular calculations, a reasonable approximation is to use the scaling factor for the valence shell. The Lamb shift can be estimated from the standard Darwin term with a related scaling factor. This scaling factor, which includes the factors of α , is about 0.05 for H, and drops to 0.025 for the first row and 0.015 for the second row elements. The estimate is probably accurate to about 10%. Although this is a small factor relative to the Darwin term, there is a cancellation between the mass–velocity term and the Darwin term, so that as a fraction of the scalar relativistic contribution, the Lamb shift could be much larger.

In this Letter we investigate the magnitude of the Lamb shift for some atomization energies in

which the scalar relativistic contribution is chemically significant. The series of molecules chosen for investigation is BF_3 , AlF_3 , and GaF_3 . The central atom in each of these molecules has a sizeable change in the s populations from the atom to the molecule, and hence an appreciable scalar relativistic contribution to the atomization energy.

Geometries for the three molecules were optimized at the hybrid [14] B3LYP [15] level using the 6-31++G* basis set [16,17] for all atoms. GAUSSIAN 98 [18] was used for the B3LYP calculations. The calculations of atomization energies were performed at the Hartree–Fock (HF) and averaged coupled-pair functional [19] (ACPF) levels of theory, using the computer program MOLPRO [20], which has been modified to produce Lamb shift estimates in addition to the mass–velocity and Darwin (MVD) scalar relativistic corrections to the energy. A single reference configuration was used in the ACPF calculations, in which only the valence electrons were correlated except for Ga for which the 3d electrons were correlated as well. The cc-pVTZ basis set of Dunning and coworkers [21–23] was used for B and Al, and the aug-cc-pVTZ basis set for F. For Ga, the CV(tz) basis set [24] was used.

The results of the calculations are presented in Table 1. In addition to the values in the contracted basis set at the B3LYP geometries, calculations were done at the experimental geometry [25] for BF_3 and with an uncontracted basis set for BF_3 and GaF_3 . The MVD estimates are known [26] to be sensitive to the contraction. For BF_3 a 10% variation was observed, in both the MVD contribution and the Lamb shift contribution to the atomization energy, but for GaF_3 the sensitivity was markedly smaller. The Lamb shift is 5% of the scalar relativistic contribution to the atomization energy for BF_3 and AlF_3 but only 2.5% for GaF_3 . In all cases, the Lamb shift estimate is much smaller than the target of chemical significance of 1 kcal/mol, but if the target is a few tenths of a kcal/mol, as is the case in more recent highly accurate calculations [3,4], the Lamb shift becomes a contribution which must be taken into account.

This leads us to consider the issue of the circumstances under which the Lamb shift might be chemically significant. We are considering here

Table 1
Contribution to the atomization energies in kcal/mol of BF₃, AlF₃ and GaF₃ at the HF and ACPF levels of theory

Geometry/basis	HF			ACPF			
	NR	MVD	Lamb	NR	MVD	Darwin	Lamb
BF ₃							
B3LYP/cont.	372.337	-0.969	0.047	451.841	-0.816	1.813	0.042
B3LYP/uncont.	372.689	-0.881	0.045	451.101	-0.665	1.632	0.038
Exp./cont.	373.454	-0.967	0.048	451.920	-0.819	1.844	0.043
AlF ₃							
B3LYP/cont.	325.985	-1.539	0.073	407.555	-1.236	3.103	0.065
GaF ₃							
B3LYP/cont.	243.693	-8.489	0.211	329.635	-7.393	14.906	0.191
B3LYP/uncont.	244.067	-8.583	0.212	328.436	-7.468	14.941	0.191

only the issue of the magnitude of the contribution to a process, so that a decision can be made about whether or not to include the Lamb shift. Naturally, if there are larger errors in a calculation due to omission of other important effects, the inclusion of the Lamb shift in the calculation is not necessary.

The major contribution to the Lamb shift comes from atoms that have a large change in *s* orbital population, in the same way as for scalar relativistic effects. Any energy that has a large scalar relativistic contribution is therefore a candidate for a significant Lamb shift.

One kind of process that has a large scalar relativistic contribution is atomization energies of halogen-containing species, which are of interest in semiconductor manufacture. For molecules in which there are several atoms which have a large change in *s* population, the Lamb shift could ac-

cumulate to produce a significant contribution. The contribution to the atomization energy of CF₄, for example, might be only 0.05 kcal/mol, but in the perfluoroalkane series, this contribution would have to be multiplied (approximately) by the number of carbon atoms in the molecule.

For heavy elements the scalar relativistic contributions can be large, and the Lamb shift will undoubtedly make chemically significant contributions to molecular energetics. For example, the MVD estimate of the scalar relativistic contribution to the energy of the reaction PbH₄ → PbH₂ + H₂ is 14 kcal/mol. This is almost certainly an underestimate, and the true scalar relativistic contribution is likely to be closer to 25 kcal/mol. The perturbation estimate of the Lamb shift would be between 0.35 and 0.7 kcal/mol. This is also probably an underestimate, not only because of the breakdown of perturbation theory,

Table 2
Relativistic correction to the atomization energies in kcal/mol of BF₃, AlF₃ and GaF₃ at the HF and ACPF levels of theory

Geometry/basis	HF		ACPF	
	DKH	MVD	DKH	MVD
BF ₃				
B3LYP/cont.	-0.881	-0.969	-0.716	-0.816
B3LYP/uncont.	-0.875	-0.881	-0.713	-0.665
Exp./cont.	-0.880	-0.967	-0.716	-0.819
AlF ₃				
B3LYP/cont.	-1.611	-1.539	-1.338	-1.236
GaF ₃				
B3LYP/cont.	-8.857	-8.489	-8.059	-7.393

DKH: Douglas–Kroll–Hess method; MVD: mass–velocity and Darwin perturbation method.

but also because the Lamb shift starts to increase again for the heavier elements. Contributions of the order of 1 kcal/mol are therefore likely for heavy element reaction energies.

In the heavy element regime, the perturbation estimate of the energy, both the scalar relativistic and the Lamb shift, is no longer adequate, and more sophisticated methods must be used for both. Even for light atoms the scalar relativistic contribution is better estimated by a method such as the Douglas–Kroll–Hess method [9,10]. This method is more stable than the MVD method, as can be seen from the results in Table 2, but does not lend itself easily to the calculation of the Lamb shift. It is clear that further developments are necessary in order to take the Lamb shift into account more reliably.

In conclusion, we find that the Lamb shift is not very large for the test cases selected here, but is large enough to make its consideration mandatory in accurate calculations whose target is a few tenths of a kcal/mol. Additionally, it is likely to be as large as 1 kcal/mol in processes involving heavy elements.

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