Estimation of Lamb-shift effects for molecules: Application to the rotation-vibration spectra of water

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(Received 7 August 2000; published 12 January 2001)

A simple approach is presented for approximating Lamb shifts, the leading quantum electrodynamical (QED) effects, in molecules containing light elements. The Lamb-shift contributions to the electronic energies are estimated from scaled nuclear and electronic Darwin terms. QED effects on the rovibrational states of water are found to be significantly larger than current experimental uncertainties, and only one order of magnitude smaller than current computational uncertainties.

DOI: 10.1103/PhysRevA.63.024502 PACS number(s): 31.30.Jv

The purpose of this paper is to make three points: (1) For relatively light atoms the Lamb shift, the leading quantum electrodynamic (QED) effect, can be estimated straightforwardly from the nonrelativistic electron density; (2) precision of quantum chemical treatments applied to predict thermochemical data or rovibrational spectra of small molecules has become so high that it is now worth discussing QED effects; (3) the highly excited rotational and vibrational states of water are a good candidate for seeing the Lamb-shift effects. Accurate measurements are available, and the molecule is sufficiently small for accurate calculations and important.

The precision of the best electronic structure calculations is now so high that they require kinetic relativistic corrections during computation of thermodynamic and spectroscopic properties of all molecules. For elements up to the third row (Na–Ar), first-order perturbation theory with the Dirac-Pauli Hamiltonian is adequate. Its three one-electron parts, for an effective potential $V(\mathbf{r})$ (in atomic units),

$$H^{\mathrm{Pauli}} = -\frac{\alpha^2}{8}\mathbf{p}^4 - \frac{\alpha^2}{8}\nabla^2 V - \frac{\alpha^2}{4}\boldsymbol{\sigma}\cdot(\nabla V)\times\mathbf{p}, \qquad (1)$$

are called the mass-velocity, Darwin, and spin-orbit contributions, respectively. For light closed-shell molecules, the mass-velocity plus Darwin (MVD) approximation is an excellent one. For a Coulomb potential $\nabla^2 V = -4Z\pi\delta(\mathbf{r})$.

The relativistic effects on the valence properties of the various elements are now largely known [1] and grow roughly like Z^2, where Z is the full nuclear charge. For the sixth-row (Cs–Rn) and heavier elements, they become large enough to explain many of their unique chemical and physical properties, as compared with lighter analogs. In highly accurate calculations they are relevant for all elements.

What has not been considered for molecules of chemical interest is the treatment of physical effects beyond the Dirac-Coulomb-Breit approximation. These leading Lamb-shift contributions are the vacuum polarization and self-energy terms, both formally of order α^3. For the light systems H_2 and H_2^+ both the experimental and theoretical accuracies are very high and the (small) leading Lamb-shift terms have long been evaluated and found relevant [2–6]. They decrease the D_0 of H_2 by 0.2 cm^{-1} and shift its vibrational band origins by a maximum of 0.02 cm^{-1} per Δv [4].

Although the QED effects for high-Z few-electron atoms had been intensively studied [7–9], little information is available for neutral or nearly neutral atoms beyond lithium, or for their compounds. The recent calculations [10,11] for the s^1 atoms Li-$E119$ and Cu-$E111$ suggested that for the heavier elements ($Z>50$) the Lamb shift cancels about 1% of the kinetic effects. For the lighter elements this Lamb/Dirac ratio for the first ionization potential increases to -8.75% for the lithium $2s$ shell [12]. *Then the Lamb shift becomes the leading correction after the Breit-Pauli one, and is comparable with its smaller terms.*

Here we use a very simple device for evaluating it. As stated by Bethe and Salpeter [13], the total Lamb shift for s electrons can be approximated as

$$E_1^{\mathrm{Lamb}} = \frac{4\alpha^3 Z}{3}\left[-2\ln(\alpha Z) - \ln X + \frac{19}{30}\right]\langle\delta(\mathbf{r})\rangle. \qquad (2)$$

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TABLE I. Values of $F(Z\alpha)$ for valence orbitals for $Z=1$ to 54.

Z	n	$F(Z\alpha)$	Z	n	$F(Z\alpha)$	Z	n	$F(Z\alpha)$
1	1	10.3168	19	4	3.6770	37	5	2.6228
2	1	8.5283	20	4	3.5834	38	5	2.5885
3	2	7.7357	21	4	3.4960	39	5	2.5558
4	2	7.0249	22	4	3.4142	40	5	2.5246
5	2	6.4848	23	4	3.3374	41	5	2.4949
6	2	6.0523	24	4	3.2654	42	5	2.4666
7	2	5.6937	25	4	3.1975	43	5	2.4396
8	2	5.3892	26	4	3.1336	44	5	2.4139
9	2	5.1257	27	4	3.0732	45	5	2.3893
10	2	4.8944	28	4	3.0162	46	5	2.3660
11	3	4.7470	29	4	2.9622	47	5	2.3438
12	3	4.5631	30	4	2.9110	48	5	2.3226
13	3	4.3970	31	4	2.8626	49	5	2.3024
14	3	4.2461	32	4	2.8166	50	5	2.2833
15	3	4.1082	33	4	2.7729	51	5	2.2651
16	3	3.9816	34	4	2.7314	52	5	2.2478
17	3	3.8649	35	4	2.6919	53	5	2.2314
18	3	3.7569	36	4	2.6544	54	5	2.2159

For hydrogenlike atoms $X=2K_{n0}/(\alpha Z)^2=11.77$, 16.64, 15.93, 15.64, and 15.16 for $1s$, $2s$, $3s$, $4s$, and ∞s, respectively [8], where K_{n0} is the Bethe logarithm. Assuming that its Coulomb-field values can be used for many-electron atoms, we obtain the ratio

$$E_1^{\mathrm{Lamb}}/E_1^{\mathrm{Darwin}}=\frac{8\alpha}{3\pi}\left[-2\ln(\alpha Z)-\ln X+\frac{19}{30}\right]. \qquad (3)$$

This equation gives the *s*-state Lamb shift as a renormalized Darwin term. Such a ratio was already given by Bjorken and Drell [14] in the form

$$E_1^{\mathrm{Lamb}}/E_1^{\mathrm{Darwin}}=(8\alpha/3\pi)\ln(1/Z\alpha). \qquad (4)$$

A slightly different approach is to start from the self-energy expression

$$E_1^{\mathrm{SE}}=\alpha^3 ZF(Z\alpha)\langle\delta(\mathbf{r})\rangle, \qquad (5)$$

which gives the ratio

$$E_1^{\mathrm{Lamb}}/E_1^{\mathrm{Darwin}}=2\alpha F(Z\alpha)/\pi-\frac{8\alpha}{15\pi}$$
$$=(4.645\,64\times10^{-3})F(Z\alpha)-1.238\,84\times10^{-3}. \qquad (6)$$

The raw data for the function $F(Z\alpha)$ were obtained from the papers of Mohr and co-workers [15–19]. The data were fitted to a function of $Z\alpha$ after subtraction of the known analytic terms, with Bethe logarithms from Drake and Swainson [20]. The factors $F(\alpha Z)$ are quoted in Table I. Numerical values for both approaches are given in Table II. Finally we get for the two-electron term the ratio [21]

TABLE II. Values of $E_1^{\mathrm{Lamb}}/E_1^{\mathrm{Darwin}}$ for ns valence orbitals for $Z=1$ to 54.

Z	n	Eq. (3)	Eq. (6)	Z	n	Eq. (6)	Z	n	Eq. (6)
1	1	0.04960	0.04669	19	4	0.01584	37	5	0.01095
2	1	0.04102	0.03838	20	4	0.01541	38	5	0.01079
3	2	0.03385	0.03470	21	4	0.01500	39	5	0.01063
4	2	0.03029	0.03140	22	4	0.01462	40	5	0.01049
5	2	0.02752	0.02889	23	4	0.01427	41	5	0.01035
6	2	0.02526	0.02688	24	4	0.01393	42	5	0.01022
7	2	0.02335	0.02521	25	4	0.01362	43	5	0.01009
8	2	0.02170	0.02380	26	4	0.01332	44	5	0.00998
9	2	0.02024	0.02257	27	4	0.01304	45	5	0.00986
10	2	0.01893	0.02150	28	4	0.01277	46	5	0.00975
11	3	0.01802	0.02081	29	4	0.01252	47	5	0.00965
12	3	0.01695	0.01996	30	4	0.01228	48	5	0.00955
13	3	0.01595	0.01919	31	4	0.01206	49	5	0.00946
14	3	0.01504	0.01849	32	4	0.01185	50	5	0.00937
15	3	0.01418	0.01785	33	4	0.01164	51	5	0.00928
16	3	0.01338	0.01726	34	4	0.01145	52	5	0.00920
17	3	0.01263	0.01672	35	4	0.01127	53	5	0.00913
18	3	0.01192	0.01621	36	4	0.01109	54	5	0.00906

$$E_2^{\mathrm{Lamb}}/E_2^{\mathrm{Darwin}}=-\frac{14\alpha}{3\pi}\ln\alpha=0.053\,334. \qquad (7)$$

Like the Pauli approximation itself, Eqs. (3), (6), and (7) should be used only with nonrelativistic wave functions. The precision of these estimates is difficult to give, but could be of the order of a few percent. Equation (3) is expected to be too small for higher nuclear charges and even changes sign at higher Z (see Fig. 1). The $(\alpha Z)^4$ energy of the exact relativistic solution for Coulombic *s* states remains smaller than the Lamb shift (6) up to $Z=28$ [23]. With Breit-Pauli kinetic terms, the present estimates should be useful up to Ca ($Z=20$) or so. With the Dirac equation for the kinetic energy, they will be useful for even higher Z.

For practical calculations, Eq. (6) is recommended. As an example we considered here the *ab initio* prediction of the

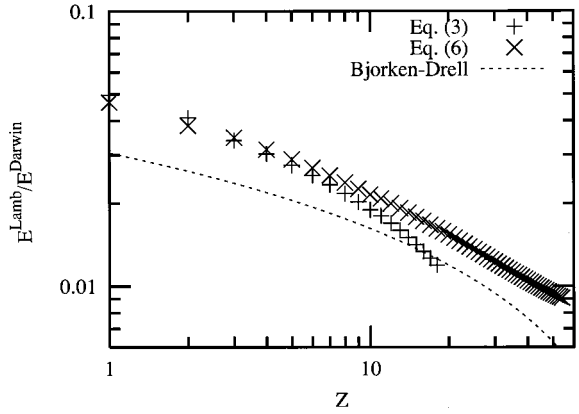

FIG. 1. The ratio $E^{\mathrm{Lamb}}/E^{\mathrm{Darwin}}$ from the present Eq. (3) and Eq. (6) and the Bjorken-Drell expression (4).

TABLE III. Sample vibrational ($J=0$) and rotational [$(v_1v_2v_3)=(000)$] energy levels of water in cm^{-1}. The one-electron Lamb-shift effects are given by Eq. (6) and the model of Ref. [26] (see text for details); observed values from the compilation of Ref. [31] are given for comparison.

Vibrational terms				Rotational terms			
(v_1,v_2,v_3)	[26]	+ Lamb	Observed	$J_{K_aK_c}$	[26]	+ Lamb	Observed
(010)	1598.19	−0.09	1594.75	20_{020}	4047.953	0.079	4048.250
(020)	3158.49	−0.18	3151.63	20_{119}	4411.989	0.085	4412.316
(030)	4677.22	−0.29	4666.79	20_{218}	4738.393	0.085	4738.622
(040)	6148.29	−0.43	6134.01	20_{317}	5031.760	0.078	5031.794
(050)	7561.09	−0.60	7542.44	20_{416}	5292.408	0.064	5292.103
(060)	8894.52	−0.86	8869.95	20_{515}	5514.246	0.027	5513.236
				20_{614}	5682.843	−0.032	5680.788
(100)	3657.68	0.18	3657.05	20_{713}	5814.138	−0.032	5812.074
(200)	7202.25	0.36	7201.54	20_{812}	5967.530	0.052	5966.823
(300)	10599.49	0.54	10599.69	20_{911}	6170.169	0.140	6170.832
(400)	13826.70	0.71	13828.28	20_{1010}	6405.763	0.207	6407.443
(500)	16986.12	0.83	16898.4	20_{119}	6661.611	0.268	6664.173
(600)	19775.79	1.01	19782.0	20_{128}	6932.041	0.328	6935.428
(700)	22519.48	1.19	22529.30	20_{137}	7213.401	0.386	7217.562
				20_{146}	7502.666	0.445	7507.545
(101)	7249.52	0.37	7249.82	20_{155}	7797.083	0.502	7802.709
(201)	10612.70	0.54	10613.35	20_{164}	8093.994	0.560	8100.291
(301)	13829.31	0.71	13830.94	20_{173}	8390.721	0.617	8397.648
(401)	16896.50	0.83	16898.84	20_{182}	8684.412	0.676	8691.927
(501)	19776.00	1.01	19781.10	20_{191}	8971.828	0.735	8979.881
(601)	22519.69	1.19	22529.44	20_{200}	9248.924	0.797	9257.459
(701)	25105.51	1.29	25120.28				

rovibrational states of water, where not only is the accuracy of the electronic structure calculations [24,25] high but the MVD terms have a substantial effect on the rovibrational eigenspectrum [26].

The Lamb shift as a function of geometry was evaluated using the molecular E_1^{Darwin} energies of Ref. [26] which were scaled by Eq. (6) (Table I) to obtain E_1^{Lamb}. While the two-electron Darwin and one-electron Lamb terms are comparable, the two-electron Lamb terms (7) never exceeded 0.05 $cm^{-1}$and were neglected. CCSD(T)/cc-PVQZ wave functions were used. The Lamb shift raises the electronic total energy of water at its equilibrium geometry by 1064.1 cm^{-1}. The barrier to linearity of water, the subject of considerable recent *ab initio* attention [29], is lowered by 3.88 cm^{-1}. This contribution to the total energy is comparable with the Breit value of 1663 cm^{-1} [27].

Calculations on the rotational and vibrational states of water were performed using the best available *ab initio* Born-Oppenheimer (BO) potential [24] augmented by a mass-dependent adiabatic or Born-Oppenheimer diagonal correction (BODC) [28] and a relativistic surface [26]. Nonadiabatic effects were partially allowed for by using a hydrogenic mass midway between the nuclear and atomic values [28]. This model corresponds to the best one used by Császár *et al.* [26].

Nuclear motion calculations were performed with the DVR3D program suite [30] to an accuracy sufficient for all figures quoted. Sample energy levels for $H_2{}^{16}O$ calculated with and without the Lamb-shift contribution are presented in Table III. Although the shifts are small in many cases, they are significant in some. For example, the vibrational band origin of the ''bright state'' (501), which is more accurately represented in local mode notation as $(50)^-0$, shifts by almost 1 cm^{-1}; this is 10^3 times the experimental error with which this level has been determined [31]. Similarly, the 20_{200} rotational level is shifted by more than 0.7 cm^{-1}, some 500 times the present experimental accuracy [31], which in this case could be improved by up to three orders of magnitude using current technology. The Lamb-shift effect increases with increasing excitation both for the vibrations and for the rotations.

Although our predicted contributions due to the Lamb shifts are in all cases significant compared to experimental accuracy, they are smaller than the accuracy of presently available *ab initio* techniques. It is therefore necessary to consider the sources of error in our potential-energy surface. Our *ab initio* calculation is underpinned by the following components: the BO potential, the BODC, the kinetic relativistic correction, and the nonadiabatic correction. Two of these, the BODC and the kinetic relativistic correction, are accurate to better than the contribution of the Lamb shift, a view confirmed by independent calculation of these quantities [24,27]. The dominant source of error arises from the nonrelativistic BO potential [24,26]. While such quantum

chemical calculations can be improved by larger basis sets and higher level of electron correlation, the nonadiabatic corrections are more problematic. Our use of effective masses is taken from procedures developed for diatomic systems. It is possible to use the effective mass to test the magnitude of this correction. Small changes in the effective mass for the $(0n0)$ bending states give shifts similar in magnitude to the QED effects on these states. However, for the stretching modes the shifts due to QED effects were found to be much larger, usually by an order of magnitude. Thus the functional forms of the nonadiabatic and QED effects are different. Furthermore, both the BODC and nonadiabatic effects are mass dependent and their contribution can be characterized using isotopic substitution.

In conclusion, we present a straightforward method for estimating the leading quantum electrodynamical effects in light molecules. This correction may increase the physical accuracy of the best quantum chemical calculations by an order of magnitude. Improvements in procedures for computing the *ab initio* Born-Oppenheimer potential energy surface for the electronic ground state of water should lead to the situation where the much studied spectrum of water can be used as a probe of Lamb-shift effects.

This work was supported by The Academy of Finland, the Hungarian Scientific Research Fund, the Hungarian Ministry of Education, the Hungarian-British Joint Academic and Research Program, the U.K. Engineering and Physical Sciences Research Council, and the Russian Fund for Fundamental Studies.

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