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Comment on "The adiabatic approximation"

J.F. Ogilvie¹

A. Mickiewicz University, Department of Theoretical Chemistry, ul. Grunwaldzka 6, PL 60-780 Poznań, Poland

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Abstract

Nonadiabatic effects are compared with adiabatic effects in their influence on the equilibrium bond length and harmonic vibrational wavenumber of diatomic molecules. The relative accuracies of results of spectrometric experiments and quantum-chemical computations are briefly discussed in relation to adiabatic and nonadiabatic effects.

Handy and Lee [1] presented results of quantumchemical calculations of inferior accuracy (only at the so-called SCF level, relative to accurate coupled-cluster or r_{12} methods to which they allude [1]) about the effects of finite nuclear mass on molecular properties.

In their equation (1) based on work of Born and Huang [2] rather than the refined and extended treatment of Fernandez [3],

$$\left(-\frac{1}{2}\sum_{A}v_{A}^{2}/M_{A}+U_{n}(X)-W\right)\psi_{n}(X) = -\sum_{A}\sum_{n'}C_{nn'}(X, \nabla_{A})\psi_{n'}(X).$$
(1)

Handy and Lee [1] include terms for both adiabatic effects, within $U_n(X)$ on the left side, and nonadia-

batic effects, on the right side. These authors [1] state "For the moment these [i.e. the nonadiabatic effects] are ignored, justified by the usual perturbation theory argument that assumes no near degenerate electronic state". We present here explicit evidence about the relative magnitudes of adiabatic and nonadiabatic effects deduced from spectral analyses [4–6].

For LiH, an instance of a light molecule with no electronically excited state particularly near the ground state of interest, our previous work [4] demonstrates that adiabatic contributions to molecular eigenvalues have magnitudes comparable to nonadiabatic contributions, even at energies corresponding to only the first few vibrational states and hence far from the dissociation limit. As illustration we compare adiabatic and nonadiabatic contributions, represented in auxiliary term coefficients Z_{kl} , with mechanical effects (reflecting purely a potential-energy function, intrinsically including 'relativistic' effects dependent on internuclear distance) represented in the principal term coefficients Y_{kl} , accord-

¹ Address from September 1996: Oregon State University, Department of Chemistry, Corvallis, OR 97331-4003, USA. E-mail: ogilviej@ccmail.orst.edu

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ing to a formula for vibration-rotational eigenvalues or spectral terms [7]

$$\tilde{E}_{vJ} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \left(Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} + Z_{kl}^{r,a} + Z_{kl}^{r,b} \right) \\ \times \left(v + 1/2 \right)^{k} \left[J(J+1) \right]^{l}$$
(2)

in which denotation of isotopic dependence of \tilde{E}_{uJ} , Y_{kl} and all Z_{kl} is suppressed; coefficients Y_{kl} contain implicitly the reduced mass μ to various powers, whereas Z_{kl} contain implicitly (for a diatomic molecule having disparate nuclear charges) the mass of atomic centre either A or B, according to the superscript. To compare with the harmonic vibrational wavenumber $\omega_e \approx Y_{1,0} \sim 1.3 \times 10^5 \text{ m}^{-1}$ of ⁷Li¹H, for ⁷Li the adiabatic contribution -4.7 m^{-1} to $Z_{1,0}^{\nu}$ tends to cancel the nonadiabatic contribution 3.7 m^{-1} , but for ¹H these contributions, -40 and -11.5 m^{-1} respectively, are additive; the latter values correspond to about a tenth the "super high accuracy" mentioned by Handy and Lee [1]. In relation to the principal rotational parameter $Y_{0,1} \approx$ $B_e \sim 660 \text{ m}^{-1}$ of ⁷Li¹H, adiabatic and nonadiabatic contributions, -0.051 and 0.046 m^{-1} respectively, to $Z_{0,1}^r$ tend also to cancel for ⁷Li but to add for ¹H, being -0.33 and -0.31 m⁻¹ in the same order [4]; either latter value corresponds to a variation about 4×10^{-14} m in R_e or again about a tenth the accuracy described by Handy and Lee [1]. This comparison demonstrates that contributions of nonadiabatic effects to observable properties in at least some molecules, even light molecules, are definitely not negligible relative to adiabatic effects. (For $Y_{1,0}$ the applicable nonadiabatic effects are vibrational, whereas for $Y_{0,1}$ the applicable nonadiabatic effects are rotational.) Moreover, as atomic - not nuclear masses are employed in analysis of the spectra [4], the use of atomic masses clearly does not make nonadiabatic effects vanish.

For a relatively massive molecule such as SiS other conditions emerge. Reduction of spectral data to reproduce 3025 spectral lines of multiple isotopic variants within the accuracy of their measurement requires only twelve parameters [8]. When two of these (related to $Z_{0,1}^r$) are constrained to values consistent with the known electric dipole moment and rotational g factor (which is a measure of nonadiabatic rotational effects [7,9,10]), no adiabatic contri-

bution to $Z'_{0,1}$ is detectable; as before, atomic – not nuclear – masses are employed exclusively during inversion of the spectral data. Thus nonadiabatic effects in relation to R_e are here much more important than adiabatic effects, although the former, not the latter, were ignored by Handy and Lee [1]. Such a small contribution of adiabatic effects that vary with R in relatively massive molecules (both atoms with atomic number > 10) is a common phenomenon [5,6,11], even though theoretical justification of this empirical observation is lacking [9].

Present evidence indicates that the ratios of adiabatic and nonadiabatic effects (in a given Z_{kl}) to mechanical effects (in the corresponding Y_{kl}) are, as expected, of the order of the ratio of electronic to nuclear masses (i.e. at most about 1/1860 for ordinary nuclides) [4-6]. As the "super high accuracy" of bond lengths (such as ~ or > 2.5×10^{-13} m for a bond length about 10^{-10} m) described by Handy and Lee for calculations of molecular electronic structure [1] is still relatively at best about 1/400, even greater accuracy of computations must be attained before consequences of adiabatic and nonadiabatic effects become significant, and likewise for "harmonic and fundamental [vibrational] frequencies", regardless whether atomic or nuclear masses are employed to calculate these quantities.

The values of the "diagonal Born-Oppenheimer correction" for H₂, HF, N₂ and F₂ [1], presented to at least five digits, are not directly verifiable from experiments. As the values in the same table [1] calculated for R_e (given in nine digits) and ω_e (in six digits) differ from values from experiments [12] in their second or third digits, the reliability of this "correction" to the stated precision is suspect.

In summary, the accuracy of calculations of molecular electronic structure, not merely the results of Handy and Lee [1] but other quantum-chemical calculations of purported great accuracy [1], relative to results from experimental techniques even other than spectrometric, such as X-ray crystallography and electron diffraction, is questionable. Spectrometric measurements can yield an accuracy of the equilibrium internuclear separation R_e (from which all dependence on isotopic mass is, within experimental error, eliminated) that is currently limited more by uncertainties of fundamental physical constants h and N_A than by error propagated from measurements

of frequencies or wavenumbers of spectral transitions. Even so, the (single) standard error associated with R_e can generally attain a range less than $2 \times$ 10^{-16} m; for the origin of the fundamental band $\tilde{\nu}_0$ or the hypothetical harmonic vibrational wavenumber $Y_{1,0}$ (= $U_{1,0}/\mu^{1/2}$) $\approx \omega_e$ the standard error is typically less than 0.03 m⁻¹; for instances of such results see Refs. [11] for nonhydrides and [13] and [14] for hydrides. These uncertainties are about one thousandth the errors of the "super high accuracy predictions" mentioned by Handy and Lee [1]. Development of methods to treat properly not only adiabatic but also nonadiabatic (as well as relativistic and radiative) effects would hence be desirable and timely, but only after the performance of conventional quantum-chemical computations is substantially improved, so that meaningful comparison with exemplary spectral data becomes practicable. For species of which spectra with well resolved rotational fine structure are not yet recorded, quantumchemical calculations might provide rough predictions, which might assist planning or interpretation of experiments.

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