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Articles

Adiabatic and nonadiabatic effects in molecules made easy

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Adiabatic corrections to the potential energy curve, and the nonadiabatic correction to the ground-state vibrational level of the H_2 molecule, are introduced on simple qualitative grounds, so that they can be taught in basic Molecular Physics and Quantum Chemistry courses. Despite the approximations used, the quantitative corrections are quite close to their known values, yielding corrections within 10–20% of accurate values, so that their qualitative motivations are a didactically useful outcome, giving lecturers and students a clear physical interpretation of the motion in molecules beyond the drastic clamped-nuclei approximation.
Keywords: Molecular Quantum Mechanics, Adiabatic Correction, Nonadiabatic Correction.

1. Introduction

The ongoing field of molecular spectroscopy [1], especially when applied to small (primordial) molecules, becomes a real challenge for theoretical researchers and, at the same time, for lecturers in undergraduate and graduate quantum physics and chemistry courses. The experimental accuracy is so high, under $10^{-1} - 10^{-2}$ cm^{-1}, that the traditional Born-Oppenheimer approximation [2, 3], which presents errors of dozens of cm^{-1} in the energy levels, is no longer sufficient to explain the measurements. Corrections beyond the Born-Oppenheimer approach are necessary to account for these measurements, the more important being the so-called *adiabatic*, *nonadiabatic* , and *relativistic* corrections. Although the last is qualitatively quite reasonable to explain in class, despite relativistic calculations other than for one-electron molecules [4] being not easy (but much smaller for the H_2 molecule), the first two involve concepts and formalism that are usually mastered only by experts. Note that standard textbooks like [5] usually cover the BO approximation but not beyond it.

Here I try to reduce this instructional gap via approximate developments, which are qualitatively justified and are also possible to perform in standard quantum calculations through only simple changes. The hydrogen molecule, H_2, is used for simplicity, but the ideas and calculations are relatively easy to extend to two-electron diatomic molecules. Basic books in this field, such as [5, 6], can then benefit from the developments reported here.

To achieve this goal, semi-qualitative approaches are applied to adiabatic and nonadiabatic corrections of the H_2 molecule in its ground state. The adiabatic correction is introduced as the well-known reduced mass effect in the hydrogen atom, while the nonadiabatic correction is simulated by means of a model in which nuclei drag electrons along their vibrations. These approximations are easily understood by students in quantum physical chemistry courses.

2. Theoretical Background

For teaching purposes, and considering the level of the discipline, this section can be followed in detail or simply reduced to the main ideas at the instructor's discretion.

The adiabatic approximation is a cornerstone of molecular physical-chemistry, since it permits the separation of electronic and nuclear motions in a creative way, originally proposed in the works of Born and Oppenheimer [2], using a perturbative approach, and later by Born and Huang [3], with a variational approach. For present purposes, the Born-Huang formalism is the main reference, though the nomenclature continues to honour the seminal Born-Oppenheimer work [2]. The main idea is that the slow nuclei move in the instantaneous mean field of the fast electrons, providing a proper basis for the cited separation of motions. The electronic problem is then solved considering only a parametric dependence on the nuclear coordinates. The resulting electronic energy plus that of nuclear repulsion provide a potential for the nuclear movement. In what follows, atomic units, a.u., ($\hbar = 1$, electron charge $e = 1$, electron mass $m = 1$ and electrostatic constant $(\frac{1}{4\pi\varepsilon_0}) = 1$ are used, but the symbol m is kept for clarity.

The two nuclei and the two electrons are referred to, respectively, as A and B, and 1 and 2. The nonrelativistic Hamiltonian for a homonuclear diatomic

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molecule, and particularly for H_2, can be written as

$$\hat{H} = \hat{T}_N + \hat{H}_{BO}, \tag{1}$$

where $\hat{T}_N$ is the kinetic energy operator for the A and B nuclei,

$$\hat{T}_N = \hat{T}_A + \hat{T}_B = -\frac{\nabla_A^2}{2M} - \frac{\nabla_B^2}{2M}, \tag{2}$$

where M is the mass of a hydrogen nucleus in a.u.

$\hat{H}_{BO}$ is the electronic clamped-nuclei Born-Oppenheimer Hamiltonian, which contains the kinetic energy of the electrons, all potential energy terms involving electrons, $\hat{V}_{el}$, and the nuclear repulsion term $\frac{1}{R}$, in which the internuclear distance R plays, at this stage, just the role of a parameter, not of a dynamical variable,

$$\hat{H}_{BO} = -\frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} + \hat{V}_{el} + 1/R. \tag{3}$$

In the Born-Huang theory [3], the full wavefunction of the system is written as a linear combination of previously obtained electronic states ϕ_i, see equation (6) below. Here, restriction is made to the simplest problem, in which the electronic ground-state is well separated from the other states so that the so-called *one-state approximation*, which corresponds to the adiabatic approximation, stands. In quantum mechanical terms, the molecular wavefunction of the H_2 molecule in its ground-state is written as

$$\Psi(R, r) = \phi(R; r)\chi(R). \tag{4}$$

The semicolon stands for parametric dependence of ϕ on R, meaning that R is fixed in particular nuclear configurations while r stands for free electronic coordinates. The product function, equação (4), allows separation into an electronic factor $\phi(R; r)$, and a nuclear one $\chi(R)$, obtained as follows.

Ψ must satisfy Schrödinger's time-independent equation,

$$\hat{H}\Psi(R, r) = E\Psi(R, r), \tag{5}$$

where E is the total ground-state energy of H_2, $\chi(R)$ is still unknown, and the nuclear wavefunction $\phi(R; r)$ is normally obtained as an eigenfunction of the Born-Oppenheimer Hamiltonian,

$$\hat{H}_{BO}\phi(R; r) = \varepsilon(R)_{BO}\phi(R; r). \tag{6}$$

This equation is solved for a grid of values of R ranging from near zero to large ones, close to molecular dissociation. The term $\frac{1}{R}$ in equação (3) guarantees that $\varepsilon(R)$ is repulsive at short nuclear distances, while the remaining terms have an attractive behavior, yielding a Morse type function of R, see Figure 1.

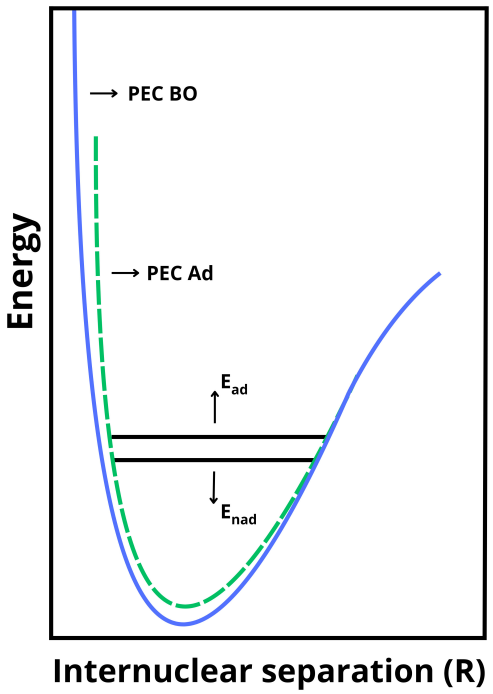

Figure 1: The picture has only illustrative purposes, no real scale or dimension should be taken. Recall that adiabatic corrections amount about 100 cm^{-1} while nonadiabatic corrections are about 0.5 cm^{-1} large. PEC BO and PEC Ad represent, respectively, Potential Energy Curves in the Born-Oppenheimer and in the Adiabatic approximations. E_{ad} and E_{nad} represent, respectively, an adiabatic and the corresponding nonadiabatic energy levels.

Having in hands the electronic state, $\phi(R; r)$, an equation for the motion of the nuclei is then obtained as follows.

In order to eliminate translation, moving the reference frame from the laboratory (LAB) to another fixed in the molecule (MOL) is necessary. Despite being trivial, this is not a straightforward step, but details can be seen by interested readers in [7]. Here a coordinate system with origin in the center-of-mass of the nuclei [7] is chosen. The molecular kinetic energy operator changes from the form of equação (2), which is restricted there to two electrons, to,

$$\hat{T}_N = -\frac{\nabla_R^2}{2\mu_N} + \sum_{i,j} \frac{\overrightarrow{\nabla}_i \cdot \overrightarrow{\nabla}_j}{2M}, \tag{7}$$

in which $\mu_N = \frac{M}{2}$ is now the reduced mass of the nuclei and (i, j) represent electrons in an multi-electron molecule. Note that if molecular rotations were considered, the resulting MOL reference frame would be non-inertial, producing quite small effects on the results, but this is not the case here.

Aiming at solving equação (5), the action of this operator on Ψ, equação (4), must be considered. A known property of the Laplacian leads to (from now

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on the arguments of the wavefunctions are dropped, for simplicity),

$$\nabla_R^2(\phi\chi) = \phi\nabla_R^2\chi + \chi\nabla_R^2\phi + 2\overrightarrow{\nabla}_R\phi\cdot\overrightarrow{\nabla}_R\chi. \quad (8)$$

Provided $\phi(R;r)$ is normalized for each value of R, $\langle\phi|\phi\rangle = 1$, it results that $\overrightarrow{\nabla}_R\langle\phi|\phi\rangle = 0$. A simple manipulation yields $\langle\overrightarrow{\nabla}_R\phi|\phi\rangle + \langle\phi|\overrightarrow{\nabla}_R\phi\rangle = 0$, so taking ϕ as a real function (if ϕ is complex, it may always be multiplied by a phase that makes it real), $\langle\phi|\overrightarrow{\nabla}_R|\phi\rangle = 0$. Thus, the last term in equação (8) vanishes.

Inserting the above developments into equação (5) finally yields, after some manipulation,

$$\left[-\frac{\nabla_R^2}{2\mu_N} - \langle\phi|\frac{\nabla_R^2}{2\mu_N} + \sum_{i,j}\frac{\overrightarrow{\nabla}_i\cdot\overrightarrow{\nabla}_j}{2M}|\phi\rangle + \varepsilon_{BO}(R)\right]\chi(R) = E_{ad}\chi(R). \quad (9)$$

This is the adiabatic Schrödinger equation for the nuclear motion. In the clamped-nuclei Born-Oppenheimer approximation, $\hat{T}$ is neglected so that the second term in the left-hand-side of equação (9) vanishes. Clearly $\varepsilon_{BO}(R)$ acts then as a potential energy curve for the nuclear states. These states are called ro-vibrational, since the molecule can vibrate and rotate but here only nuclear vibrations are considered, focusing on the ground-state of H_2, with energy E_{ad}. This equation is easily solved using standard methods for the radial Schrödinger equation, such as LEVEL [8], thus yielding the Born-Oppenheimer evaluation of E and $\chi(R)$. Equação (4) gives then the full molecular wavefunction.

What if the one state adiabatic approximation for Ψ, equação (4), is kept but the nuclear kinetic energy is not neglected? In this case the second term in equação (9) is a correction to the potential energy curve, $\varepsilon_{BO}(R)$, the so-called *Diagonal-Born-Oppenheimer-Correction* (DBOC), or simply the *adiabatic correction*,

$$DBOC = -\langle\phi|\frac{\nabla_R^2}{2\mu_N} + \sum_{i,j}\frac{\overrightarrow{\nabla}_i\cdot\overrightarrow{\nabla}_j}{2M}|\phi\rangle. \quad (10)$$

It should be noted that DBOC becomes a function of R after bracketing it with ϕ, the electronic wavefunction. The word "diagonal" refers to the Born-Huang expansion of the molecular wavefunction in multiple terms $\phi_k\chi_k$, using the Born-Oppenheimer set of solutions ϕ_k, a multiple-state approach that leads to a set of coupled nuclear equations for the χ_k. This approach, which explicitly includes the nonadiabatic coupling terms, demands unnecessary efforts to the present purposes, but a clue to their formal origin is easy to understand as follows.

Consider a multiple-state approach, $\Psi = \sum_k\phi_k\chi_k$, where the ϕ_k are again eigenstates of the Born-Oppenheimer Hamiltonian and the χ_k are unknown nuclear functions. In a development quite similar to the previous one, the first term on the right-hand-side of equação (8) gives rise to *diagonal* (adiabatic) terms on the basis ϕ_k, e. g., $\langle\phi_k|\nabla_R^2|\phi_k\rangle$ or *non-diagonal* (nonadiabatic) terms, e. g., $\langle\phi_k|\nabla_R^2|\phi_l\rangle$. The resulting equations for nuclear motion are coupled by these last terms so that the whole set of equations must be solved simultaneously. In such an approach the concept of a single potential energy curve loses its meaning, of course.

Both the adiabatic and the nonadiabatic corrections, as formally introduced, have no simple interpretations. Moreover, they are very difficult to calculate, so that going beyond Born-Oppenheimer becomes a challenge for teaching or didactic texts. In this article, approximate approaches for the adiabatic and nonadiabatic corrections to the ground energy of the H_2 molecules are introduced, aiming at filling this gap.

3. The Adiabatic Correction

Suppose that moving from the LAB to the MOL reference frame is made, approximately, by postulating that the linear momentum $\overrightarrow{p}$ is conserved in each H atom, instead of in the molecule. In this case, $\overrightarrow{p}_A$=-$\overrightarrow{p}_1$ or, equivalently, $\overrightarrow{\nabla}_A = -\overrightarrow{\nabla}_1$, $\nabla_A^2 = \nabla_1^2$, analogously for atom B and electron 2. The nuclear kinetic energy, equação (2), can then be written in terms of electronic operators only and can thus merge with the Born-Oppenheimer electronic kinetic energy. Inserting these results in the molecular Hamiltonian, equação (1), with the help of equações 2 and 3, yields (recall that $m = 1$ in a.u.),

$$\hat{H} = -\frac{\nabla_1^2}{2m} - \frac{\nabla_1^2}{2M} - \frac{\nabla_2^2}{2m} - \frac{\nabla_2^2}{2M} + \hat{V}_{el} + 1/R = -\frac{\nabla_1^2}{2\mu} - \frac{\nabla_2^2}{2\mu} + \hat{V}_{el} + 1/R, \quad (11)$$

where μ now stands for the nucleus-electron reduced mass. It is notable that, except for the repulsive terms, the above Hamiltonian resembles that of two separate H atoms moving in their proton-electron center-of-mass reference frames, in which the known reduced mass effect appears.

Note also that in this approximation, $\hat{H}$ is *per se* the new electronic Hamiltonian, whose ground eigenstate $\phi(R;r)$ is obtained in a Born-Oppenheimer-like calculation just changing m to μ,

$$\hat{H}\phi(R;r) = \varepsilon(R)\phi(R;r) \quad (12)$$

and whose eigenvalue $\varepsilon(R)$ is the very potential energy curve for nuclear motion. On the other hand, it contains information of the nuclear motion through the reduced mass effect.

The adiabatic correction, $\triangle\varepsilon_{ad}$, no longer has the form of an added term, as in equação (9). Instead, it

is now built into the total Hamiltonian, but can be evaluated as,

$$\triangle\varepsilon_{ad} = \varepsilon - \varepsilon_{BO}. \tag{13}$$

The adiabatic correction is an R-dependent quantity. Evaluating it in a standard quantum chemical calculation for both $\hat{H}$ and $\hat{H}_{BO}$, at the H_2 equilibrium distance $R_{eq} = 1.4$ Bohr, gives $\triangle\varepsilon_{ad} = 101.2$ cm^{-1}, to be compared to DBOC= 114.6 cm^{-1} [9].

The difference on the order of 10% is not even just an error, since the comparison involves two quantities having little different definitions, $\triangle\varepsilon_{ad}$ and DBOC . In fact, the larger the distance R, the more exact is ε, since the system becomes two separated H atoms, for which the present kind of correction (different from DBOC) is exact. The conclusion strikes the eyes: *The adiabatic correction is, to a great extent, the electron reduced mass correction.* This point is little known, even among experts in the field. It appears as a consequence of moving from the LAB to the MOL reference frame. It seems proper here to give Nicholas Handy the recognition to be the first to have suggested it, see, for example [10].

4. The Nonadiabatic Correction

It was previously argued that nonadiabatic effects can be introduced by coupling different Born-Oppenheimer electronic states. The picture of electrons being transferred among molecular electronic states (perhaps, from one atom to another) in chemical reactions, matches qualitatively the formalism. In this case, however, nonadiabatic coupling terms can be huge, and calculations are in no way straightforward. But what happens if the electronic ground-state is so isolated from the others that electrons do not really move around in the molecule, but only go just "a little along with their own nuclei"? The motion is no longer adiabatic, but still occurs in a single potential energy curve, that is, allowing to keep the one-state approximation. This is exactly what happens with the well isolated ground-state of the H_2 molecule.

The answer to the above question is quite simple, despite having been ignored for long time: The nonadiabatic character means exactly "not adiabatic", that is, the electrons do not really adapt their motion instantaneously to the nuclear motion. They must move along with the nuclei while they vibrate (and, more generally, though not here, rotate). A possible reason for why this picture has been ignored for a long time seems to be that it implies the nuclei dragging R-dependent *fractional parts* of a single electron along with their motion, as in the case of the molecular ion H_2^+, for example. But this possibility is not forbidden by quantum theory anyway! In fact, it is this very idea that allowed the currently most accurate calculations of nonadiabatic corrections to primordial molecules [11]. On the other hand, it seems reasonable that, for beginners, the simpler picture of each electron following a nucleus all the way along the zeroth-order vibration of H_2 is more appropriate. For this, it is enough to replace, in the first term of equação (9), μ_N with μ_{At}, the *atomic reduced mass*, defined by,

$$\mu_{At} = \frac{M+1}{2}. \tag{14}$$

This means that the electron mass (= 1) is added to the nuclear masses to constitute the moving units in the molecular vibration. The idea can again be traced back to Handy and Lee [10], but the artifice seems to be used for the first time in nonadiabatic calculations by Zobov et al. [12]. The nuclear equation then becomes,

$$\left[-\frac{\nabla_R^2}{2\mu_{At}} - \langle\phi|\frac{\nabla_R^2}{2\mu_N} + \sum_{i,j}\frac{\overrightarrow{\nabla}_i\cdot\overrightarrow{\nabla}_j}{2M}|\phi\rangle + \varepsilon_{BO}(R)\right]\chi(R) = E_{ad}\chi(R). \tag{15}$$

The presence of the DBOC, the second term of this equation, is in fact only formal. It is enough to use the Born-Oppenheimer potential energy curve $\varepsilon_{BO}(R)$ (or even $\varepsilon(R)$ from the approach in the previous section) to proceed. Once the curve is available, equação (15) is easily solved with the help of the well known computational package LEVEL [8]. The nonadiabatic correction $\triangle E_{nad}$ is a single number that must be added to E as a correction, a very small one in fact. It is obtained simply by the difference,

$$\triangle E_{nad} = E_{ad} - E_{nad}. \tag{16}$$

Once again, a simple picture works well in view of that the accurate nonadiabatic correction to the ground vibrational level of H_2 is -0.499 cm^{-1} [14], while the present approach gives -0.588 cm^{-1}. Remarkably, the correct order of magnitude is obtained and the relative error is about 20%. There are more sophisticated approaches for the effective nuclear masses, which contains R-dependent fractions of the electron mass [11], but the one used here, e. g., the atomic mass, is undoubtedly the simplest.

The central idea of changing the nuclear reduced mass to account for nonadiabatic effects has developed over time, but recognizing that this effect would be related to the addition of fractions of electron mass to the nuclear masses was first proposed by Kutzelnigg [13].

5. Final Remarks

It is known that the adiabatic approximation preserves the separation of the nuclear and electron motions based on their very different intrinsic time scales, thus preserving the idea of a potential energy curve. This is done by taking into account the kinetic energy of the nuclei while solving the electron problem. What seems to be less known is the equivalence of this quantity, meaning DBOC, with the effect of introducing the

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electron reduced mass in the full Hamiltonian. Although adding to ε_{BO} the bracket of the nuclear kinetic energy with the electronic wavefunction, see equação (9), looks like an awkward procedure, at least for students, the reduced mass effect is well known since their first studies of the H atom.

As for the nonadiabatic effects, these can also be introduced in simple terms: The dragging of fractions of electrons by the nuclei in their motion. It should be noted that this assumption does not compromise the adiabatic separation, which is made previously and generates the potential energy curve for nuclear motion. In fact, an effective nuclear reduced mass, μ_{At} in the present case, applies just to the nuclear kinetic energy operator in equação (15). Again, the qualitative interpretation of the nuclei having a slightly greater effective mass due to fraction of electrons dragged along with them replaces, in didactic terms, the difficult formal concept of nonadiabatic effects.

The effects studied here are illustrated in Figure 1, though no scale or magnitude can be associated to it. The adiabatic correction, a "kinetic energy", is obviously positive and a function of R, so the potential energy curve is raised (hundreds of cm^{-1}) a little from the Born-Oppenheimer curve, as shown by the dashed green curve. In turn, the nonadiabatic correction is normally a negative number that will be added to E, lowering it by a very small amount (units of cm^{-1}).

Beyond the simple qualitative interpretation, another aspect of the proposed applications is the possibility of performing them in common quantum chemical calculations. The adiabatic correction, introduced simply by repeating a Born-Oppenheimer calculation with μ replacing the electron mass in the kinetic energy terms, has little dependence on electronic methods, so basic book exercises with two-electron diatomic molecules can be upgraded to perform it. Care must be taken, however, if the chosen method uses the linear combinations of atomic orbitals (LCAO) technique, which can involve mixture of orbitals centered on different atoms. In this case, in view of the procedure of approximate momentum conservation in each atom, the corrections involving matrix elements of $\hat{T}_{AorB}$ between orbitals centered on *different* atoms must vanish [15]. In turn, the nonadiabatic correction is even simpler, since the reduced nuclear mass is normally an input quantity in methods to solve the radial Schrödinger equation [8]. It is independent of whether or not the adiabatic correction is performed to the potential energy curve, being applicable to a clamped-nuclei Born-Oppenheimer calculation as well, with no detectable change in its value.

As a classroom application, students can obtain a PEC for the H_2 molecule on the Hartree-Fock level, compute its ground vibrational energy with the reduced mass correction using equação 15 to assess the improvement toward the experimental dissociation energy.

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Data Availability

The data that support the findings reported in this study are contained in the text.

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