Electronic vibration in molecules.

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Abstract

We show how to extract information from the usual programs of molecular structure, regarding the wavefunctions representing electronic vibration (and rotation) in molecules, due to the following by the electrons of the nuclei in their motion.

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1 Introduction

Bill Meath used to say that his main purpose in publications was to "point new things out", rather than to present a more accurate calculation on a worn-out problem. This is the spirit of the present work, which focuses on an useful insight that was obtained in previous articles [1, 2, 3], by establishing connections between molecular spectroscopy and molecular dynamics. The connections are based on two common grounds:

1) The total hamiltonian of a molecule is identical to the hamiltonian of a collision between a portion of the molecule with the remainder part. The only differerence lies in the asymptotic boundary conditions of the corresponding Schrödinger equation, which are plane-wave and spherical-wave-type for a scattering problem, and exponentially decaying for the bound states of molecular spectroscopy. This point is explicited in detail e.g. in ref. [4] for electron impact on ions *v.* electronic radiative transitions, and in ref. [5] for atomic collisions *v.* the spectroscopy of diatomic molecules.

2) There is a parallelism between the practical methods employed to study collisional and spectroscopical problems, employing the Born-Oppenheimer (BO) approximation [6, 7], as a starting point.

The subject matter here refers to a shortcoming of the standard BO approximation that had first been pointed out in dynamics [8], and then in vibration e.g. in refs. [9, 10, 11, 12, 13]. The usual set up in which this subject arises refers to "rigorous" approaches that go beyond the aproximation, and inevitably involve time-consuming calculations carried out with expansions over large sets of electronic and nuclear functions. These calculations are routinely employed in dynamics (where the number of relevant references is huge, see e.g. reviews in refs. [14, 15]), whereas the applications to vibration are much scarcer (see e.g. ref. [16] for the simplest molecule, H_2^+). In fact, most work on the subject of non-BO calculations on bound problems focus on the topic of adiabatic (diagonal) corrections to the spectroscopic frequencies (e.g. [17, 18, 19, 20]), and is not directly connected to our subject matter.

As mentioned above, our aim here is not to present an even more accurate non-BO calculation on a vibrational problem. We shall point out that the run-of-the-mill wavefunctions obtained in routine calculations provide useful information on the molecular structure that is in fact beyond BO; and we shall prove by explicit examples that the procedure involves a minimal computational work, and certainly does not require that one should be familiar with the methods of molecular dynamics. For the sake of simplicity of presentation, we restrict our illustrations to the ground electronic state of the hydrogen molecular ion and to only three vibrational states, but it will be clear that our procedure is immediately applicable to any molecular orbital, or configuration interaction wavefunction, and to any normal (or local) mode, of any molecular system.

In addition to this main point, we show that the procedure can represent what is in principle an observable effect, and which does not relate to the extremely accurate calculations of non-adiabatic corrections. The effect is a contribution of the electronic vibration to the electronic density: besides their contribution to the forming of the chemical bonds, electrons also vibrate (and rotate) as they follow the nuclei in their motion; and the wavefunction representing the electronic vibration contribute to the total electron density [16]. Our point here is that this effect can be gauged off-hand from standard, reasonably accurate orbitals, without the need of time-consuming calculations. If sizeable, the effect could be observed in the near future, by using the developing sources that emit attosecond bursts of X-ray to study, and control, the motion of electrons inside atoms [21].

2 The nature of the Born-Oppenheimer approximation

It is obvious that when one considers the structure of molecules, one is not only talking about the electronic density. The visualization programs that are nowadays available not only provide electronic energies for fixed nuclear configurations, as well as other properties such as dipole moments, etc., but also a (slowed down) picture of normal mode vibrations. In turn, this picture can be in terms of wire-and-ball models (then, the balls vibrate) or sticks (the bonds vibrate). While the usefulness of these pictures as a complement to a blackboard exposition is undeniable, one can then ask how does this picture honestly reflects the actual theory employed in the calculations carried out by the "package" program, rather than, e.g., the programmer's imagination.

One is then led to consider the nature of the Born-Oppenheimer approximation, in which the molecular wavefunction Ψ is factorized in a nuclear part χ, times an electronic part ϕ, which is obtained by solving the Schrödinger equation for fixed nuclei:

$$\Psi(\mathbf{r},\mathbf{R}) = \chi(\mathbf{R})\ \phi(\mathbf{r};\mathbf{R}) \tag{1}$$

where $\mathbf{r}$ stands for all electronic coordinates, and $\mathbf{R}$ for all nuclear ones, and:

$$H(\mathbf{r};\mathbf{R})\phi(\mathbf{r},\mathbf{R}) = E(\mathbf{R})\phi(\mathbf{r};\mathbf{R}) \tag{2}$$

with H the usual clamped-nuclei Hamiltonian. $E(\mathbf{R})$ is the electronic energy, which is the well-known PES for the nuclear motion.

The physical basis of the approach is that, given the large nuclear masses (in atomic units), to treat the electronic motion one can take the slowly moving nuclei as fixed. This was originally developed in ref. [6] in terms of a double series: a power series in $M^{-1/4}$, with M the mean mass of all the nuclei, and a series in the nuclear displacements about the equilibrium position. The advantage of using $M^{-1/4}$ rather than $M^{-1/2}$ is that the zeroth-order vibrational equations are solved analytically in terms of the harmonic oscillator eigenfunctions. To sum up, the accuracy of the BO approximation stems from the larger value of M, and the correction terms are $\mathcal{O}(M^{-1/2})$.

In practice, rather than ref. [6], what has been found more useful is the treatment given in the Appendix of the book by Born and Huang [7], where Ψ is expanded in tems of the (in principle) complete set of electronic wavefunctions for fixed nuclei :

$$\Psi_j(\mathbf{r},\mathbf{R}) = \sum_n \chi_{jn}(\mathbf{R})\ \phi_n(\mathbf{r};\mathbf{R}) \tag{3}$$

Introduction of this expansion in the Schrödinger equation then yields a system of coupled differential equations for the nuclear wavefunctions. The so-called *non-adiabatic* coupling terms are essentially written in terms of nuclear gradient transition matrix elements: $\langle\phi_n|M_\alpha^{-1}\nabla_{\mathbf{R}_\alpha}|\phi_m\rangle\cdot\nabla_{\mathbf{R}_\alpha}\chi_{jm}(\mathbf{R})$. For bound systems, when they are neglected, eqs. (1) and (2) hold, and one obtains a set of uncoupled equations for the vibro-rotational functions χ_{jn}; introduction of weighted coordinates and expansion about the equilibrium configuration (a local minimum of $E(\mathbf{R})$), yields, in a standard fashion, the normal-mode description of vibration. Since $\nabla_{\mathbf{R}_\alpha}\chi = \mathcal{O}(M_\alpha^{1/2})$ (consider, e.g., harmonic oscillator wavefunctions), the coupling term is $\mathcal{O}(M_\alpha^{-1/2})$, in agreement with the perturbation treatment of ref. [6]. An alternative approach to the Born-Huang procedure has been employed by Bishop and Cheung for H_2^+ [16], and is in terms of expansions over sets of *analytical* electronic and nuclear wavefunctions, which has several computational advantages.

Born-Huang type approaches have found extensive applications in dynamical problems, and expansions over large numbers (e.g., hundreds) of molecular states are nowadays commonly employed to treat collisional problems up to impact energies so high that one or more electrons are ejected. Incidentally, we note that the original method of ref. [6] is inapplicable to those problems, because there is a reaction coordinate along which some nuclei are displaced by arbitrarily large amounts. In collisional problems, the nuclear wavefunctions contain plane-wave-type functions like $\exp(ik_\alpha M_\alpha R_\alpha)$, so that $\nabla_{\mathbf{R}_\alpha}\chi = \mathcal{O}(M_\alpha)$, the coupling terms are $\mathcal{O}(M_\alpha^0)$, and are therefore usually more sizeable than in spectroscopy. They can give rise to transitions, and integration of the asymptotic values of the corresponding probabilities yields the cross sections for non-radiative transitions, and thence the corresponding reaction constants.

We now mention what is essentially wrong in the description of vibration by eq. (1), even when one is not aiming at spectroscopic accuracy. While in its description of vibrorotational motion, what move are the nuclei, since the electronic structure parametrically depends on the nuclear positions (this is the meaning of the semi-colon in $\phi_n(\mathbf{r};\mathbf{R})$), it must also change when the nuclei move. Hence, electrons also vibrate (and rotate): in other words, what *really* vibrate are the atoms, i.e., the bonds. However, there is no wavefunction in eq. (1) depicting the vibrational motion of the electrons. Turning now to the exact treatment of eq. (3), it turns out that this motion is represented by fictitious (virtual) transitions to an infinity of electronic states, through the coupling terms $\langle\phi_n|M_\alpha^{-1}\nabla_{\mathbf{R}_\alpha}|\phi_m\rangle\cdot\nabla_{\mathbf{R}_\alpha}\chi(\mathbf{R}) = \mathcal{O}(M_\alpha^{-1/2})$. Similar transitions also describe finer effects, such as the tiny delay between the nuclear motion and the following of the electronic cloud (the cloud lags a little behind) [1]. Moreover, when the matrix elements

$\langle\phi_n|M_\alpha^{-1}\nabla_{\mathbf{R}_\alpha}|\phi_m\rangle$ are large, the delay can give rise to important *observable* effects, such as non-radiative transitions to bound (spectroscopical perturbations) or continuum (predissociation) states. For diatomic molecules, they are well documented in the literature [22], and will not be treated here. The mixture of observable and unobservable effects induced by the same couplings is the unsatisfactory feature of the usual BO formulation.

This feature also gives rise to a well-known formal difficulty of molecular spectroscopy, which we briefly comment upon; for more quantitative presentations, see e.g. refs. [9, 10, 23]. When the velocity, or minimal coupling, form of the radiation-matter hamiltonian is employed in the derivation of the radiative transition probability together with BO wavefunctions (1), one incorrectly finds that the electronic part of these wavefunctions, $\phi(\mathbf{r};\mathbf{R})$, does not contribute to the infrared line intensities. On the other hand, use of the dipole formulation for the radiation-matter interaction hamiltonian yields the correct, usual form of the Einstein coefficient [9, 10, 23]. As is well known, both formulations are equivalent for exact wavefunctions, and are related through a gauge transformation. The anomalous result for the former is sometimes dubbed a "paradox", because use of a conmutator expression that only holds for exact wavefunctions allows to retrieve the correct result for the velocity formulation. Then, introducing an approximate step helps to get the correct answer, which seems surprising.

When one analyses the problem in detail, one finds that what is wrong in the BO formulation is that it yields vanishing transition matrix elements of the total electronic momentum, whereas they do not vanish for the exact wavefunctions. From the reasoning above, we conclude that these non-zero values are due to the dragging and delay effects that are ignored in the BO approximation, so that the corresponding electronic momentum distributions are a little inaccurate. On the other hand, the electronic position distribution of the BO wavefunctions obtained from quantum chemistry is very accurate, because of the variational principle, so that the formulation in terms of dipole transition matrix elements yields the correct answer.

It was pointed out in ref. [2] that when delay effects are unimportant (that is, in most practical situations), one can palliate the problem by solving the dragging effect to lowest order in M^{-1}. The main asset of this approximate treatment is that it involves no new calculations, as explained in the following section. This solution to the problem was derived in ref. [2] by extension of standard treatment in atomic dynamics [8, 14, 24, 25, 26, 15, 27]. In this field, the fact that the BO wavefunctions (1) fail to represent the following of the nuclear motion by the electrons is even more conspicuous, and gives rise to the so-called "momentum transfer" problem. Among other difficulties, this is because, since the culprit interactions $\langle\phi_n|M_\alpha^{-1}\nabla_{\mathbf{R}_\alpha}|\phi_m\rangle \cdot \nabla_{\mathbf{R}_\alpha}\chi(\mathbf{R})$ are often nonzero even at infinite separations of the reagents, and this prevents a proper enforcement of the boundary conditions.

3 Improved formulation

We now summarise the modification of the theory that takes into account, in an approximate way, the dragging of the electrons by the nuclei. To simplify the exposition, we shall assume in the following that there are no important delay effects, that is, that there is no transition matrix element $\langle\phi_n|M_\alpha^{-1}\nabla_{\mathbf{R}_\alpha}|\phi_m\rangle$ that is very large. Then, the simplest way to improve the formulation (to lowest order in M^{-1}) in eq. (1) is to replace each nuclear coordinate $\mathbf{R}_\alpha$ by a generalization:

$$\boldsymbol{\lambda}_\alpha = \mathbf{R}_\alpha + \sum_i \ f_{i\alpha}(\mathbf{r}_i, \mathbf{R}_\alpha)\ \mathbf{r}_i \tag{4}$$

where the sum runs over all electrons, and $f_{i\alpha}$ is a mass-weighted switching function such that:

$$f_{i\alpha}(\mathbf{r}_i, \mathbf{R}_\alpha) \underset{R_\alpha \to \infty}{\longrightarrow} \begin{cases} M_\alpha^{-1} & \text{when } \mathbf{r}_i \to \mathbf{R}_\alpha \\ 0 & \text{when } \mathbf{r}_i \to -\mathbf{R}_\alpha \end{cases} \tag{5}$$

The switching function then takes the value M_α^{-1} when the ith electron travels with the α nucleus, and vanishes in the opposite direction, when this nucleus is far from the centre of the molecule. In this limit we obtain:

$$\boldsymbol{\lambda}_\alpha \to \mathbf{R}_\alpha + M_\alpha^{-1} \sum_{i\in\alpha} \mathbf{r}_i \tag{6}$$

where the sum extends to all electrons that "belong" to nucleus α when R_α is stretched in the particular normal mode considered.

One can show [27], that introduction of these "reaction" or generalized coordinates in eq. (1) eliminates the residual couplings that describe the drag effect. Eq. (1) now becomes:

$$\Psi^{\text{improved}}(\mathbf{r}, \mathbf{R}) = \chi(\boldsymbol{\lambda})\ \phi(\mathbf{r}; \mathbf{R} = \boldsymbol{\lambda}) \tag{7}$$

and the following of the nuclei by the electrons is described by the vibrorotational function $\chi(\boldsymbol{\lambda})$, which depends on $\mathbf{r}$ as well as on $\mathbf{R}_\alpha$. The notation $\mathbf{R} = \boldsymbol{\lambda}$ means that each vector $\mathbf{R}_\alpha$ is to be taken to be numerically equal to $\boldsymbol{\lambda}_\alpha$ [25]; nevertheless, in the second factor ϕ this parameter can be approximated by $\mathbf{R}$ to the lowest order in M^{-1}, and we obtain:

$$\Psi^{\text{improved}}(\mathbf{r}, \mathbf{R}) = \chi(\boldsymbol{\lambda})\ \phi(\mathbf{r}; \mathbf{R}) \tag{8}$$

These "reaction", or generalized coordinates, have been successfully employed in many calculations on ion-atom and ion-diatomic collisions. For the sake of completeness, it may be mentioned that an overwhelming amount of collisional calculations employ instead the so-called *electron translation factors* (ETFs), which are phases of the type $\exp(i\sum_i\ f_{i\alpha}\boldsymbol{k}_\alpha\cdot\mathbf{r}_i)$. In this approach, each atomic orbital making up $\phi(\mathbf{r}, \mathbf{R})$ is multiplied by an ETF. It is worth mentioning, therefore, that the ETF approach, in which electronic and nuclear motions are phase-linked [1] can be considered as an approximation to the reaction coordinate solution in the limit situation when the nuclear motion can be taken as classical, with a nuclear velocity $M_\alpha \boldsymbol{k}_\alpha$ for the α nucleus [27]. The widespread use of ETFs then stems from the accuracy and simplicity of classical trajectory calculations at high energies. At low nuclear velocities, it is better and simpler to employ the generalized coordinates.

Now, from the simple form (6) of the $\boldsymbol{\lambda}_\alpha$ coordinate, which is linear in $\mathbf{R}_\alpha$, insertion in the Schrödinger equation yields exactly the same equations for the new vibrational wavefunctions $\chi(\boldsymbol{\lambda})$ than the original BO formulation for $\chi(\mathbf{R})$; in particular, the same vibrational energies are obtained. Furthermore, the vibrational averages of line frequencies and intensities are also unchanged because the vibrational average $\int\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{R}$ is substituted by $\int\int \mathrm{d}\mathbf{r}\mathrm{d}\boldsymbol{\lambda}$. This explains the success of the BO approach. The only practical difference appears when delay effects are important and one has to take into account the corresponding non-adiabatic couplings (which are substantially modified). When they are not important, the only difference is a re-interpretation of the wavefunctions obtained, and especially the vibro-rotational component, which contains an electronic part: electrons also vibrate and rotate. As a consequence, the electronic density is modified; this effect also appears, of course, in the expansion methods, and it was exemplified in ref. [16], and found to be small, but not negligible.

4 Calculations

We now illustrate how to apply the improved formulation for the simple case of molecular orbitals, and we have chosen for this purpose the ground electronic state of the hydrogen molecular ion. For the sake of generality of the procedure, we have not employed the exact MO [28] and vibrational wavefunctions, which are available for the system considered. To represent the electronic wavefunction, we have employed a two-centre basis of 56 GTO's (11s, 8p, 5d and 4f orbitals centred on each nucleus); differences between calculated and exact energies are smaller than 1 mHartrees, which is amply sufficient for the present illustrative purposes. The vibrational wavefunctions were obtained, as explained in ref. [29] by first fitting the energy curve to a modified Morse potential, and diagonalizing the ensuing vibrational hamiltonian in a basis set of 200 one-dimensional GTO's with exponent $\alpha = 9.0$ centred on the internuclear axis at equally spaced points in the interval $0 < R < 12$ au. .

For the special case of a diatomic molecule, the formalism of section 3 yields two generalized coordinates $\boldsymbol{\lambda}_1$ and $\boldsymbol{\lambda}_2$, corresponding to the two nuclei, and the total wavefunction only depends on the difference $\boldsymbol{\lambda} = \boldsymbol{\lambda}_2 - \boldsymbol{\lambda}_1$ between these two [3], which acts as a generalized "internuclear" vector. When one employs the switching function that was proposed in ref. [30], and was employed in practically all collisional calculations of our and other groups, one obtains for the component of $\boldsymbol{\lambda}$ along the internuclear axis the simple form:

$$\lambda_z = R + \frac{2z^2}{M_H R} \tag{9}$$

which is linear in R and quadratic in the electronic coordinate z. To simplify the presentation, since by far the main effect is on the vibrational component, we choose the lowest rotational state of the molecule so that eq. (8) becomes:

$$\Psi_{1\nu}^{\text{improved}}(\mathbf{r}, R) = \chi_{\nu 00}(\boldsymbol{\lambda})\ \phi_1(\mathbf{r}; R) = (4\pi)^{-1/2}\lambda^{-1}\varphi_\nu(\lambda)\ \phi_1(\mathbf{r}; R) \tag{10}$$

while the original formulation yielded eq. (1), i.e.:

$$\Psi_{1\nu}(\mathbf{r}, R) = \chi_{\nu 00}(R)\ \phi_1(\mathbf{r}; R) = (4\pi)^{-1/2}R^{-1}\varphi_\nu(R)\ \phi_1(\mathbf{r}; R) \tag{11}$$

The main change over the usual formulation is that the usual vibrational wavefunction $\varphi_\nu(R)$ of eq. (11) is replaced in eq. (10) by $\varphi_\nu(\lambda)$, which also describes the vibration of the electrons following the nuclei. In our illustrations, we have chosen the ground vibrational state ($\nu = 0$), an intermediate case ($\nu = 6$), and a highly excited vibrational state ($\nu = 17$).

We show in fig. 1 the corresponding wavefunctions. Since the functional form of $\varphi_\nu(R)$ is identical to that of $\varphi_\nu(\lambda)$, fig. 1 can be considered to represent either wavefunction. A different matter, however, is its dependence on the electronic coordinates: while $\varphi_\nu(R)$ is obviously independent of $\mathbf{r}$ for R fixed, fig. 2 illustrates the electronic z dependence of $\varphi_\nu(\lambda)$ for $R = 2$ au., close to the equilibrium value. This dependence can be reasoned to represent electronic vibration along the internuclear axis, and is quite a simple and predictable one: the analytical behaviour can be readily obtained from fig. 1, by taking into account the $M_H^{-1}z^2$ dependence of λ_z in eq. (9). A similar information is available, of course, from either the more exact Born-Huang or Bishop-Cheung approaches (though it is not given in ref. [16]), but it requires time-consuming calculations, and would be given in terms of a superposition of a large number of electronic and nuclear wavefunctions, while obtaining fig. 1 from the usual molecular data is trivial. It is clear that the same procedure can be readily applied to molecular orbitals of polyatomic molecules, and to configuration interaction wavefunctions.

Our second point deals with the issue of whether there is an observable effect on the density due to electronic vibration. When one considers a quantitative answer to this question, one finds that the precise answer depends on the details of the particular device to be employed to measure electron densities. Up till now, what has been proposed (see e.g. the report in ref. [21]) consists in constructing a non-stationary state by superposition, and then following its evolution in real time using attosecond light pulses. The main difficulty, in the absence of a precise description of the future experiment, is that a simple generalization of the definition of electronic density is not obvious. The improved formalism yields a six-dimensional distribution $|\Psi_{1\nu}(\mathbf{r}, R)|^2$, from which one can draw, for fixed R, x, y, the values along the internuclear axis. One can then compare this to the corresponding function from the original formalism:

$$f(z) = \left|\phi_1(\mathbf{r}; R)\varphi_\nu(\lambda)\lambda^{-1}\right|^2 - \left|\phi_1(\mathbf{r}; R)\varphi_\nu(R)R^{-1}\right|^2 \tag{12}$$

However, one then finds that such a comparison can give a visually biased representation of the changes in the electronic density for excited vibrational states, mainly because of the R^{-1} and λ^{-1} factors in eq. (12). Because of this, a more useful estimate of the relative importance of the effect of electronic vibration on the electronic density is provided by a modulated difference:

$$g(z) = \left[\varphi_\nu(R)\right]^{-2} R^2 f(z) \tag{13}$$

which is displayed in fig. 3 for the same vibrational states as in the previous figures. As with fig. 2, the computational work required to obtain fig. 3 is trivial, and can be applied to any system.

We see that the main characteristics of the corrections to the electronic density displayed in fig. 3 are very similar to the qualitative ones of ref. [16] (which displays no scales in the relevant figures), and that the order-of-magnitude is similar to that cited in that reference. In addition, our approach provides a straightforward explanation of the data. The effect can be an enhancement or diminishing of the density, which is largest at the nuclear positions. While the latter feature is due to the fact that the first term in eq. (12) is proportional to $|\phi_1(\mathbf{r}; R)|^2$, the size and sign of the correction can be easily understood from fig. 4, which displays the corresponding values of $\varphi_\nu(\lambda)R/\lambda\varphi_\nu(R)$. In turn, this figure may be seen to follow from fig. 1 and eq. (9): substitution of the variable R by the new coordinate λ introduces a positive, quadratic dependence upon z; then, when $\varphi_\nu(R)$ increases with R, the result that $\varphi(\lambda) > \varphi(R)$, and the effect is an enhancement, while the opposite holds where $\varphi_\nu(R)$ decreases.

5 Concluding remarks

The present work dwells on a topic that is seldom considered by theoretical chemists, which is that the electrons must vibrate (and rotate) in molecules, as they follow the nuclei in their motion. The lack of consideration may stem from the fact that, to take into account the vibrational motion of electrons appears to require going beyond the Born-Oppenheimer approximation; and for vibrational problems this is still a formidable task for all except the simplest molecules. However, when one does not aim at spectrocopic accuracy (involving non-adiabatic corrections to the frequencies and the like), our point is that one can extract the main information on the electronic vibration in molecules very simply, and from run-of-the-mill Bohr-Oppenheimer wavefunctions.

Here we have explicitly shown how to do so, by using as an example the ground state of the hydrogen molecular ion. From the very simplicity of our calculations, we hope that it is clear that the procedure is directly applicable to any molecule, to any type of method (e.g., Hartree-Fock or configuration interaction), and to any vibrational state. The procedure only involves a calculation of the vibrational wavefunction, and substitution of the pertinent nuclear coordinates by the generalized ones (eq. (4), with any reasonable form of the switching factor). A corresponding modification of the electronic density of the molecules due to electronic vibration is then immediately obtained. In our illustrations, the density changes are very small, but measurable.

Acknowledgments

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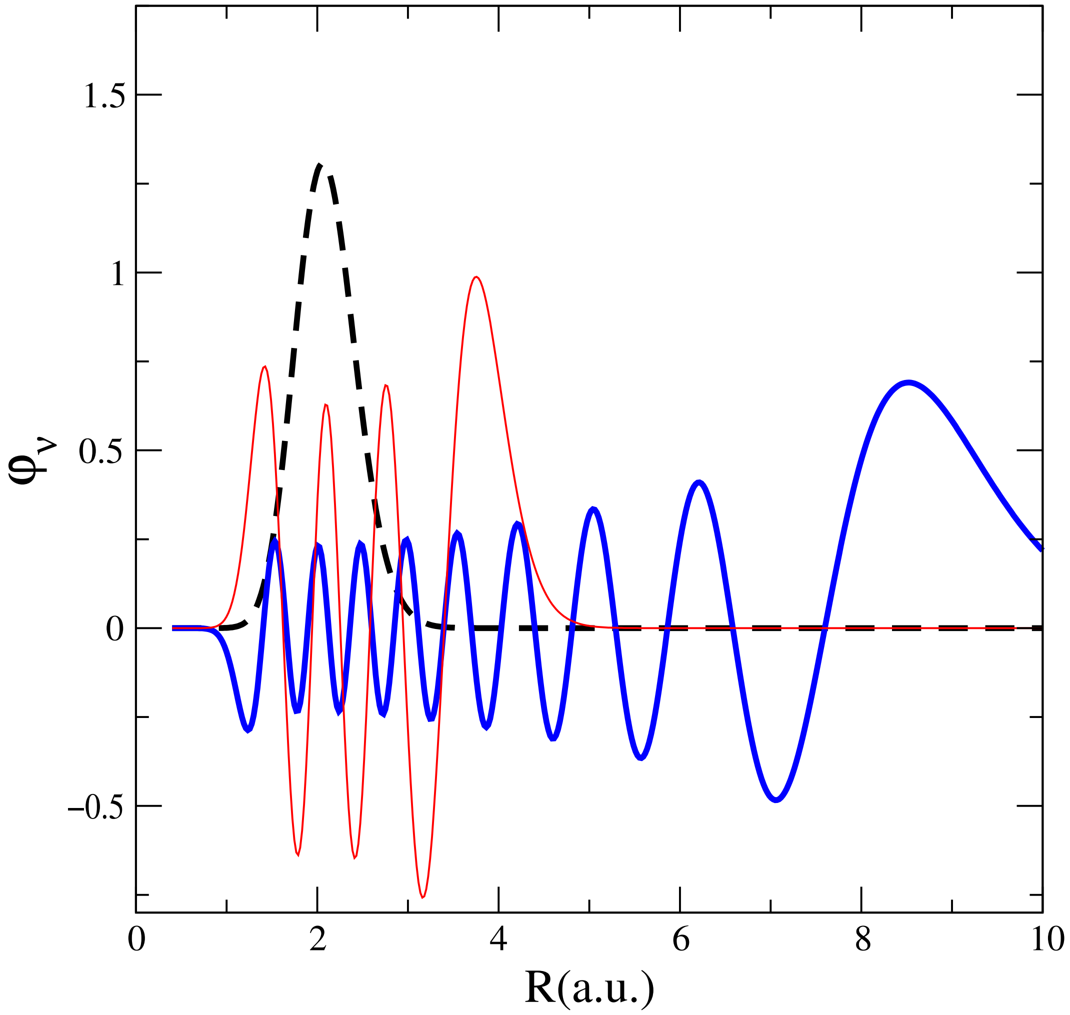

Figure 1: Values of $\varphi_\nu(\lambda)$ as functions of R for: $\nu = 0$(dashed line), $\nu = 6$(thin line), $\nu = 17$(thick line).

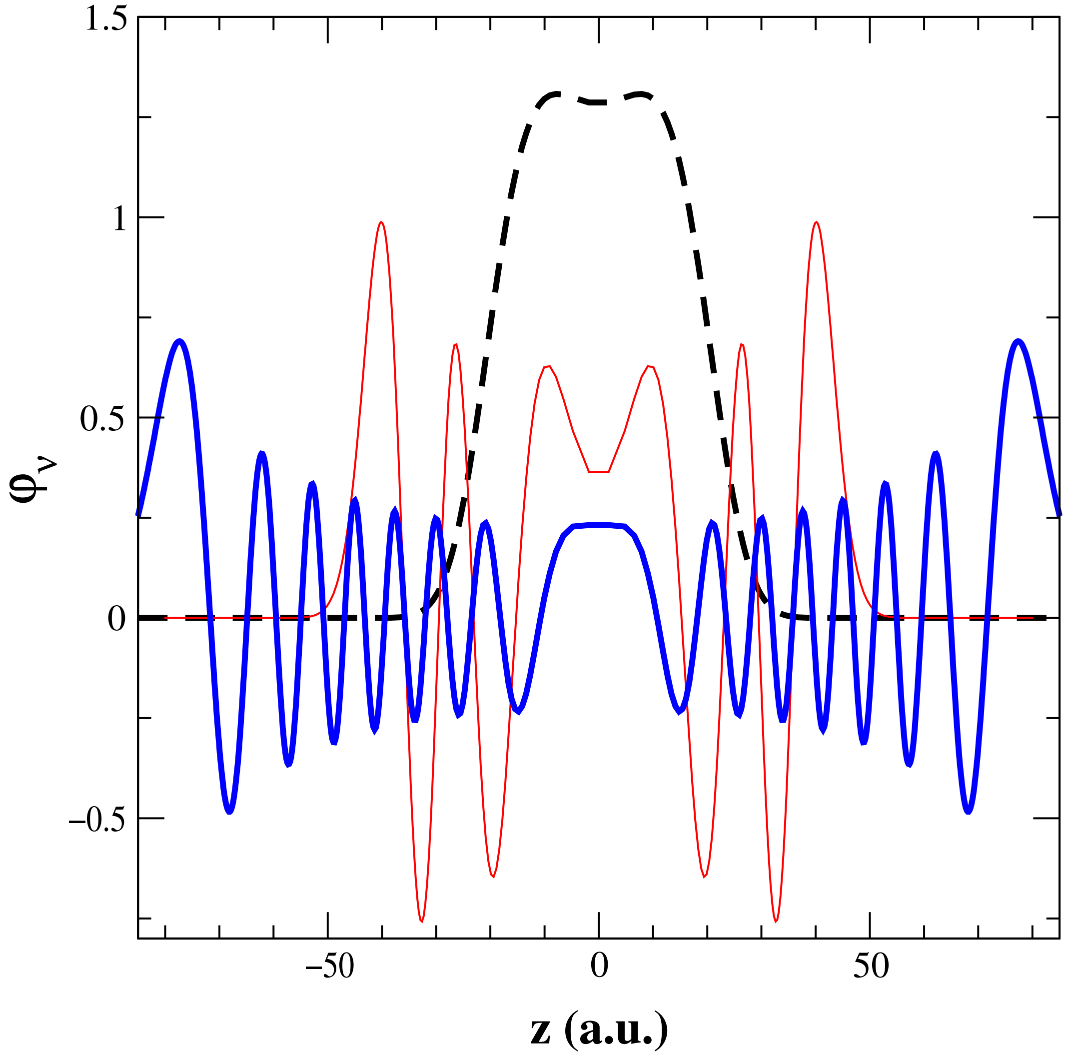

Figure 2: Values of $\varphi_\nu(\lambda)$ as functions of z for R=2.0a.u.: $\nu = 0$(dashed line), $\nu = 6$(thin line), $\nu = 17$(thick line).

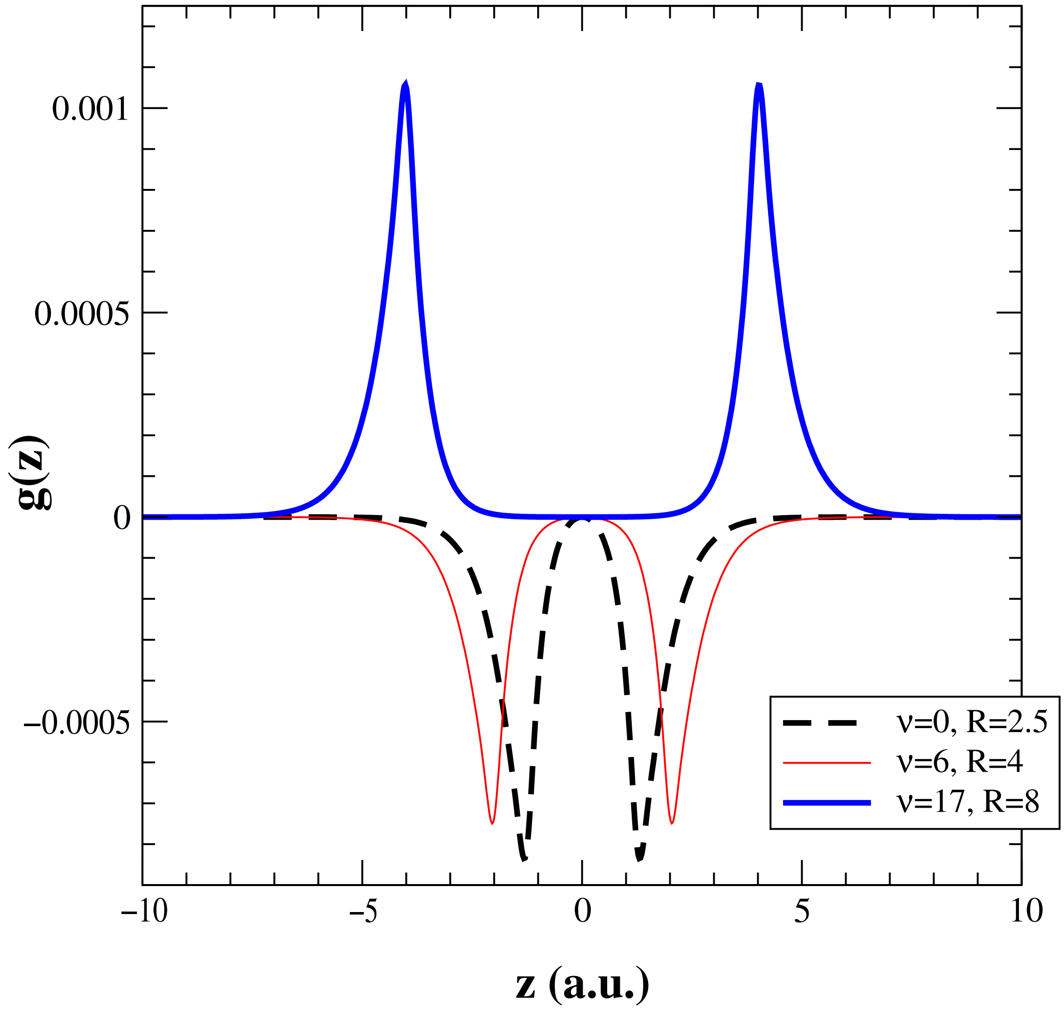

Figure 3: Values of the function $g(z)$ of eq. (13) as function of the electronic coordinate z for three vibrational states and internuclear distances: ν=0, R=2.5a.u (dashed line); ν=6, R=4a.u.(thin line); ν=17, R=8a.u.(thick line).

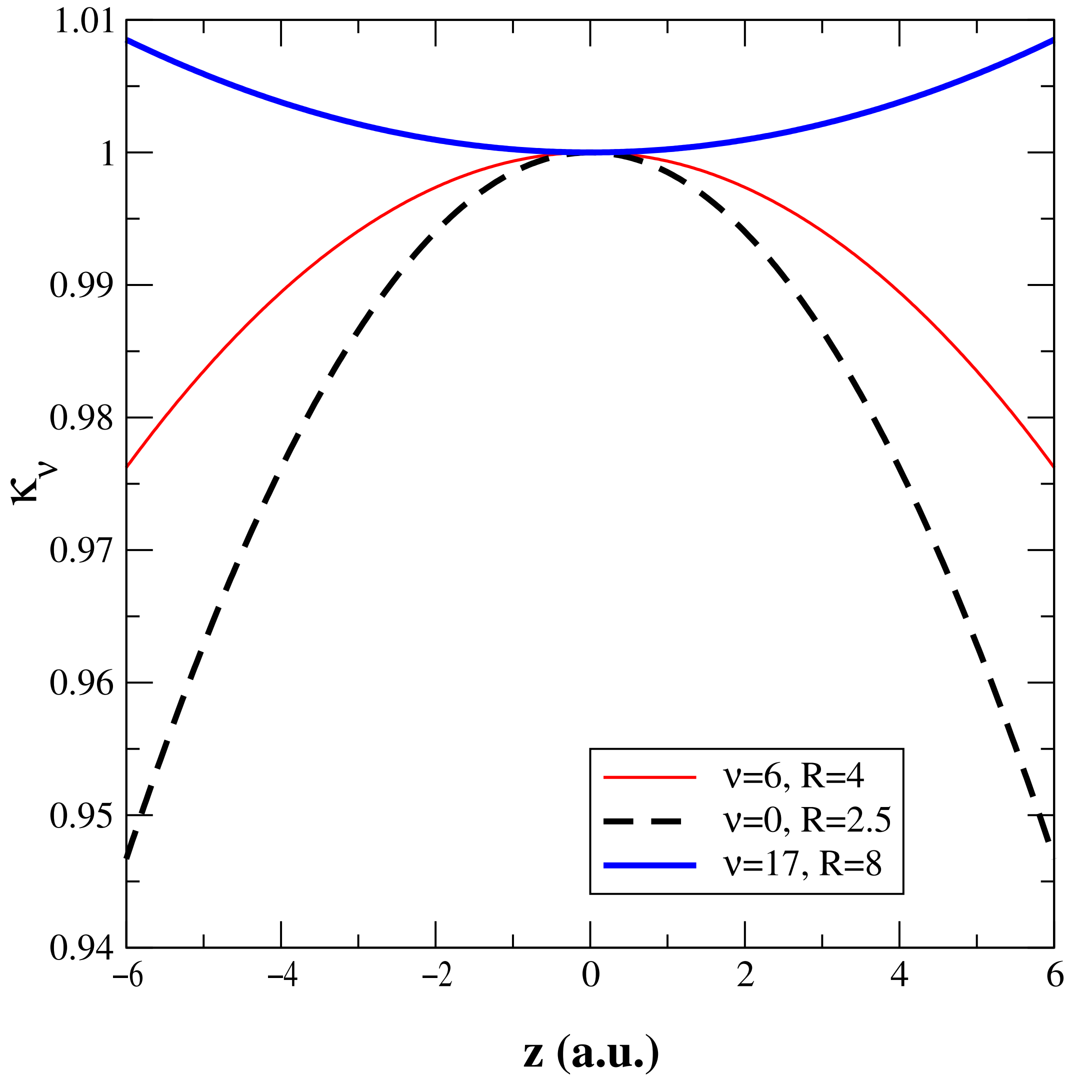

Figure 4: Values of the fractions $\kappa_\nu(z) = R\varphi_\nu(\lambda)/\lambda\varphi_\nu(R)$ as functions of the electronic coordinate z for the same vibrational states and internuclear distances as in fig. 3.