

*Review***THE GENERATOR COORDINATE APPROXIMATION FOR MOLECULES:
A REVIEW**

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Abstract

The generator coordinate approximation is a non-adiabatic theory of molecular systems. Its fundamental outlines were developed during the 1970's. A further analysis and first applications were published during the 1980's. In this paper, we review the present status of the theory.

1. Introduction

The Born–Oppenheimer approximation [1] or separation of electronic and nuclear motion is without any doubt the cornerstone of theoretical (or mathematical) chemistry and has generated the primary concepts (electronic states, potential energy surfaces, equilibrium configurations, dipole moment functions, . . .) in terms of which we talk about molecular properties.

The Born–Huang expansion [2] of the total molecular wave function in the complete set of electronic states yields a set of coupled differential equations that constitute an exact representation of the full molecular Schrödinger equation. Neglecting the coupling between different electronic states, a good approximation in the absence of (near) electronic degeneracies, leads to the so-called adiabatic approximation. The associated wave function is then a product of an electronic state and a nuclear wave function. All discrepancies (with the exact solution) caused by this approximation go under the name of "non-adiabatic effects" and are due to the fact that the nuclear kinetic energy operator is not diagonal in the electronic basis. The standard computational strategy to go beyond the adiabatic approximation is to include in the coupled equations those electronic states for which the off-diagonal matrix elements of the nuclear kinetic energy are significant. Thus improving upon the adiabatic approximation amounts to replacing a single product by a sum of products. This procedure is not satisfactory from the theoretical point of view since there is no way of estimating the convergence of the results. From a practical point of view, it turns out to be

cumbersome to calculate several electronic states to the same accuracy, i.e. it is difficult to get a balanced input for the method.

The alternative is to try to extract from a single electronic state more information than is accomplished by the adiabatic approximation. It is in this spirit that the generator coordinate approximation (GCA) was devised by replacing the product state by a convolution product. The resulting trial state in which electronic and nuclear motions are explicitly correlated (by the non-product form) can be variationally optimized and leads to the reformulation of the theory of molecules in terms of new concepts (nuclear weight function, energy integral kernels, dipole integral kernels, . . .) alternative to the traditional ones (nuclear wave function, potential energy surfaces, dipole function, . . .).

A summary of GCA theory and applications up to 1980 was given in a previous review [3]. The state of affairs at that time was the following: the formulation of the GCA theory, especially for diatomic molecules, was developed in sufficient detail to show the relevant new concepts involved, to pinpoint the computational implications. An exactly soluble test problem had shown that the GCA is capable of removing the non-adiabatic error of order κ^6 .^{*} A number of open problems could be formulated, the most immediate of which were the following:

- (1) In order to establish generally whether the GCA energetically improves the adiabatic approximation, one should carry out a full perturbation scheme (in the spirit of Born–Oppenheimer perturbation theory) of the GCA nuclear equation, i.e. the Wheeler integral equation.
- (2) To confirm the analytical results of such an analysis, a fully numerical application of the GCA to a realistic molecular system was called for.
- (3) The Dunham series [4], the term value formula that is so successful in parametrizing diatomic spectra, should have its counterpart in the GCA. The problem remained to establish the relation between the Dunham coefficients and the basic theoretical concepts of the GCA.
- (4) Although the principle involved in the GCA ansatz seemed acceptable for the energy region near a potential minimum, there was no such immediate intuitive support for the relevance of the GCA near electronic degeneracies. A test of the GCA in such cases of strong non-adiabatic effects was necessary.

Each of the open problems mentioned above has been addressed during the past decade. The present state of affairs, of which this paper gives an overview, is as follows:

- (1) A perturbation analysis of the GCA allows one to clearly distinguish between non-adiabatic contributions, of various orders in κ , to the GCA energy. Of particular importance is the propagation of inaccuracies in the input electronic state to the final GCA results.

^{*}Throughout this paper, κ denotes the Born–Oppenheimer perturbation parameter, i.e. $(m/M)^{1/4}$, where m is the electron mass and M the average nuclear mass of the molecule.

- (2) An ab-initio calculation on the H_2^+ molecule has been performed. The results confirm the theoretical findings of the GCA perturbation theory.
- (3) Using anharmonic kernel expansion and order-by-order angular momentum projection, explicit term formulae for diatomic molecules were generated. In practice, a GCA Dunham series can be established.
- (4) A two-state model for a curve crossing situation in diatomic molecules was used to test the GCA in cases of near electronic degeneracies. Numerical calculations on hydrogen and nitrogen show that the GCA effectively improves the adiabatic approximation in curve crossing problems.

The paper is organized as follows. The next section provides a general introduction to the GCA, whose main purpose is to fix the notations. Each of the following sections deals with one of the above mentioned topics. We give only the general outlines of the arguments; for details about the calculations, we refer to the original papers as quoted in the different sections.

2. The generator coordinate approximation

In this section, we give a succinct overview of the main features of the GCA. The basic assumption is the following ansatz for the total molecular wave function [5, 6]:

$$\Psi(\mathbf{r}, \mathbf{R}) = \int F(\mathbf{S} | \mathbf{W}) \varphi(\mathbf{r} | \mathbf{S}) \Phi(\mathbf{R} | \mathbf{S}, \mathbf{W}) d\mathbf{S}. \quad (1)$$

Here, \mathbf{r} stands for all the electron coordinates, \mathbf{R} for the $3N$ Cartesian coordinates of the N nuclei, \mathbf{S} for $3N$ Cartesian nuclear "generator" coordinates, and \mathbf{W} represents a set of N parameters associated with the nuclei and to be specified below. In the integrand of (1), φ is the electronic wave function. In principle, it is an exact solution of the electronic Schrödinger equation, but in practice it will only be an approximate numerical solution. The function F is called the "nuclear weight function" or "nuclear motion function". As will become clear later on, it is the analogue of the nuclear wave function in the adiabatic approximation. The factor Φ is a convolution kernel which serves to superimpose electronic wave functions at different generator positions \mathbf{S} . We assume for Φ a factorized form:

$$\Phi(\mathbf{R} | \mathbf{S}, \mathbf{W}) = \prod_{i=1}^N \phi(\mathbf{R}_i | \mathbf{S}_i, W_i). \quad (2)$$

The function ϕ is so defined that the mean value of \mathbf{S}_i is just the nuclear position

$$\int \mathbf{S}_i \Phi d\mathbf{S} = \mathbf{R}_i, \quad (3)$$

and the meaning of the parameter W_i is defined as the variance about the nuclear position \mathbf{R}_i :

$$\int (|\mathbf{R}_i - \mathbf{S}_i|)^2 \Phi d\mathbf{S} = W_i^2. \quad (4)$$

We shall henceforth refer to the parameters W_i as "width parameters". We furthermore assume that the function ϕ tends to a delta function $\delta(\mathbf{R}_i - \mathbf{S}_i)$ when the parameter W_i tends to zero. In this so-called "delta function limit", the GCA reduces to the adiabatic approximation since the convolution product (1) then goes over into the familiar adiabatic product Ψ^A ,

$$\lim_{W \rightarrow 0} \Psi = \Psi^A = \varphi(\mathbf{r}|\mathbf{R})F(\mathbf{R}). \quad (5)$$

Fundamental to the ansatz (1) is therefore the condition that the W_i are small, at least in those cases where the adiabatic approximation is already a good starting point. A physical argument for this assumption can be given by relating the correlation function Φ to a specific type of nuclear motion. Whereas the adiabatic approximation describes the nuclear motion averaged over a large number of electronic revolutions, the GCA proposes to take into account the immediate response of the nuclei to the fluctuations in electronic density. These fluctuations are much faster than the nuclear vibrations, the typical frequency ratio being of the order of κ^2 . If we assume the instantaneous nuclear motion to be harmonic, its amplitude can be estimated to be an order of magnitude smaller than the amplitude of normal nuclear vibrations. Therefore, if Φ is supposed to describe this type of motion, the width parameters W_i are expected to be of this order of magnitude. We shall show later on that this intuitive argument is corroborated by the numerical results.

The nuclear motion function F in (1) is determined by the variational principle which requires the total molecular energy to be minimum with respect to the class of trial functions of the form (1). This leads to the requirement that F be a solution of the Hill–Wheeler integral equation [7]

$$\int [\mathcal{H}(S, S'|\mathbf{W}) - E \Delta(S, S'|\mathbf{W})] F(S'|\mathbf{W}) dS' = 0. \quad (6)$$

Here, Δ and \mathcal{H} are the "Wheeler kernels"

$$\Delta(S, S'|\mathbf{W}) = \langle \varphi(S)\Phi(S, \mathbf{W}) | \varphi(S')\Phi(S', \mathbf{W}) \rangle, \quad (7)$$

$$\mathcal{H}(S, S'|\mathbf{W}) = \langle \varphi(S)\Phi(S, \mathbf{W}) | H | \varphi(S')\Phi(S', \mathbf{W}) \rangle, \quad (8)$$

where H is the complete molecular Hamiltonian. The eigenvalues E are the total molecular energies and the eigenfunctions F of (6) yield the total molecular eigenfunctions through (1) in the GCA. In regions of the spectrum where the adiabatic approximation is meaningful, F should be close to the solution F^A of the well-known adiabatic nuclear Schrödinger equation.

It should also be noted that in case the molecule contains identical nuclei, the product (2) must be symmetrized or antisymmetrized over identical bosons or fermions

in order to take care of spin statistics. Furthermore, it will be important to treat carefully the translational and rotational invariance of the total wave functions, which will require the introduction of centre-of-mass coordinates, Eulerian angles and internal coordinates.

3. Perturbation analysis of the GCA

In those regions of the spectrum where the electronic properties vary slowly with the nuclear positions, i.e. far from "avoided crossings", we may expand the electronic operators, wave functions and potentials in powers of the nuclear displacements. Born and Oppenheimer have used this technique to set up a perturbation theory for the full molecular problem [1]. In this way, they obtain a series expansion in powers of κ of the molecular energies and wave functions. Unfortunately, the perturbation expansion rapidly becomes complicated and the original Born–Oppenheimer expansion is therefore of limited practical value. However, it can still be used to determine the accuracy of more workable variational methods, such as the adiabatic approximation and the GCA, if the results of the latter can be expressed in terms of powers of κ . The Born–Oppenheimer analysis of the adiabatic approximation is well known and yields the fundamental κ^2 and κ^4 estimates of the vibrational and rotational energies and establishes an error of order κ^6 between the adiabatic and exact total molecular energies. In this section, we intend to consider similar estimates for the GCA [8,9].

3.1. PERTURBATION SERIES

In this section, we will perform the Born–Oppenheimer analysis of the GCA under the assumption that Born–Oppenheimer perturbation theory applies, i.e. that the parameter κ is small and the electronic properties vary slowly with the nuclear positions. In the present case the theory contains, in addition to κ , also the small parameters W , and therefore the analysis is more subtle.

We shall start by expressing all widths W_i in terms of one dimensionless width parameter W and length factors λ_i :

$$W_i = W \lambda_i. \quad (9)$$

The parameters λ_i are specified further by correlating them to the nuclear masses as follows:

$$\lambda_i = (M/M_i)^{1/2} a_0, \quad (10)$$

where a_0 is the Bohr radius. The scaling (10) can be justified since one expects smaller non-adiabatic effects and hence smaller W_i for heavier nuclei. The (1/2)-power in the scaling law relates the amplitude to the mass according to a harmonic motion, which may be assumed for order-of-magnitude estimates. The relations (9) and (10)

reduce the class of trial wave functions to a one-parameter family containing the single width parameter W .

Next, we define the nuclear displacement vectors \mathbf{u} by the generalized Born–Oppenheimer transformation

$$\mathbf{R}_i = \mathbf{R}_i^0 + \lambda_i \kappa \mathbf{u}_i. \quad (11)$$

Here, \mathbf{R}^0 are the nuclear equilibrium positions and the nuclear displacements \mathbf{u} are dimensionless. The transformation (11) should be regarded as a refinement of the Born–Oppenheimer transformation [1] taking into account the effect of nuclear mass difference on the vibrational amplitudes.

The assumption that W is small implies that Φ is sharply peaked as a function of $(\mathbf{R} - \mathbf{S})$. Viewed as a function of \mathbf{S} , Φ in (1) is sharply peaked around the nuclear position \mathbf{R} and falls off very rapidly when \mathbf{S} moves away from \mathbf{R} . As long as it is sharply peaked, the exact analytical form of the correlation function is of secondary importance in this respect. The remainder of the integrand of (6) varies slowly compared to Φ and we can therefore expand it in powers of $(\mathbf{R} - \mathbf{S})$ and $(\mathbf{R} - \mathbf{S}')$. Then, by using standard techniques, the integral equation (6) can be shown to be equivalent to the differential equation

$$[H_0 + \varepsilon H_1 + \varepsilon^2 H_2 + \dots] F(\mathbf{u}) = E[\Delta_0 + \varepsilon \Delta_1 + \varepsilon^2 \Delta_2 + \dots] F(\mathbf{u}). \quad (12)$$

Here, we have put

$$\varepsilon = (W/\kappa)^2. \quad (13)$$

W/κ is the ratio of the nuclear correlation length to the nuclear vibrational amplitude which, in the spirit of GCA, should be a small number. The above analysis thus suggests that ε is the natural choice of perturbation parameter in the GCA. In (12), only even powers of W occur because ϕ is even. Each power in $(\mathbf{R} - \mathbf{S})$ generates a factor W and also a factor $1/\kappa$ because of transformation from \mathbf{R} to \mathbf{u} .

The zeroth order differential operators in (12) are simply: $\Delta_0 = 1$ and $H_0 = H^A$, the adiabatic Hamiltonian. This result confirms that the GCA reduces to the adiabatic approximation in the delta function limit, i.e. when $\varepsilon \rightarrow 0$. The higher order terms in (12) contain differential operators in the nuclear displacements \mathbf{u} , e.g.

$$\Delta_1 = \langle \varphi(\mathbf{u}) | D | \varphi(\mathbf{u}) \rangle, \quad (14)$$

$$H_1 = \frac{1}{2} \langle \varphi(\mathbf{u}) | (DH + HD) | \varphi(\mathbf{u}) \rangle. \quad (15)$$

Here, the integration indicated by \langle , \rangle is over the electronic coordinates only and the dependence on nuclear coordinates is expressed in the displacements \mathbf{u} . The operator D is defined by

$$D = \sum_{i=1}^N \Delta(\mathbf{u}_i), \tag{16}$$

where $\Delta(\mathbf{u}_i)$ is the Laplacian operator with respect to \mathbf{u}_i . The n th order terms in the expansion (12) contain differential operators of $2n$ th order in the derivatives with respect to \mathbf{u} . Explicit expressions can be found in [9].

In perturbation theory, the eigenvalues and eigenfunctions of the differential equation (12) are expressed in the form of a series expansion:

$$E(\varepsilon) = E_0 + \varepsilon E_1 + \varepsilon^2 E_2 + \dots, \tag{17}$$

$$F(\varepsilon) = F_0 + \varepsilon E_1 + \varepsilon^2 F_2 + \dots. \tag{18}$$

These terms can be obtained by standard double perturbation theory [10]. We find for the zeroth order terms $E_0 = E^A$ and $F_0 = F^A$, the adiabatic values. For the first order energy, we obtain

$$E_1 = (F_0 | (H_1 - E_0 \Delta_1) | F_0), \tag{19}$$

where now the $(,)$ refer to integration over \mathbf{u} . The first order correction to the nuclear weight function F_1 is determined by the solution of the inhomogeneous equation

$$[H_0 - E_0]F_1 = [E_1 - (H_1 - E_0 \Delta_1)]F_0. \tag{20}$$

Higher order terms can be obtained by analogous formulae (see [10]).

3.2. ORDER ESTIMATES OF NON-ADIABATIC EFFECTS

So far, we have obtained a series expansion in terms of the parameter W contained in ε . What we are after, however, is an expansion in powers of κ . Therefore, it must be noted that κ is still hidden in the operators Δ_n and H_n of (12) through the following relations:

$$H = -\frac{1}{2} \kappa^2 D + H_{el},$$

$$\varphi = \sum_n \kappa^n \varphi^{(n)},$$

$$U = \sum_n \kappa^n U^{(n)},$$

where we have used H_{el} for the electronic Hamiltonian. The $\varphi^{(n)}$ are polynomials of degree n in \mathbf{u} and U is the electronic eigenvalue from

$$H_{\text{el}} \varphi = U \varphi. \quad (21)$$

Substituting the above expressions in the operators Δ_n and H_n and using the Hellmann–Feynman theorem ($\nabla = \nabla(u_i)$),

$$\langle \nabla \varphi | H_{\text{el}} | \varphi \rangle = 0. \quad (22)$$

We find for the first and second order molecular energy corrections a series expansion in powers of κ . The leading order contribution, for E_1 , is

$$A = -2\kappa^2 \langle (\nabla F_0 \cdot \nabla \varphi) | (\nabla F_0 \cdot \nabla \varphi) \rangle, \quad (23)$$

and for E_2 the leading term is

$$B = \langle (\nabla F_0 \cdot \nabla \varphi) | H_{\text{el}} - U^0 | (\nabla F_0 \cdot \nabla \varphi) \rangle. \quad (24)$$

Returning to the energy expression (17) and retaining the leading term in each coefficient E_n only, we obtain to second order for the non-adiabatic energy correction

$$\Delta E(\varepsilon) = E(\varepsilon) - E_0 = A\varepsilon + B\varepsilon^2 + \dots \quad (25)$$

So far, the parameter W and hence ε is still arbitrary. According to the variational principle, we must determine W by minimizing the total molecular energy. It follows from (25) that the optimum value of ε is

$$\varepsilon_0 = |A|/2B \quad (26)$$

and the corresponding energy gain

$$\Delta E(\varepsilon_0) = -A^2/4B. \quad (27)$$

It should be stressed here that while from (23) it follows that A is always negative, the sign of B cannot be decided in general from (24). However, for the electronic ground state it is positive. Hence, in that case, the energy $E(\varepsilon)$ has a minimum indeed. Formulae (23) and (24) show that the order in κ of A is $O(\kappa^4)$ and of B it is $O(\kappa^2)$, so the non-adiabatic energy correction is $O(\kappa^6)$, i.e. of the same order as the error on the adiabatic energy. It will be noticed that putting ε_0 in (25), both terms $A\varepsilon$ and $B\varepsilon^2$ are of the same order $O(\kappa^6)$. It can be established from the Born–Oppenheimer analysis described above that the contributions neglected in (25) are $O(\kappa^8)$ or smaller. We also conclude from the above considerations that the optimum width parameter W is $O(\kappa^2)$, consistent with the initial assumption that the nuclear correlation length is one κ -order smaller than the vibrational amplitude. Finally, it should also be observed that ε_0 is $O(\kappa^2)$, i.e. numerically of order 10^{-2} and therefore an appropriate perturbation parameter.

In numerical calculations, one necessarily works with approximate electronic wave functions. For numerically calculated electronic functions φ , the Hellmann–

Feynman theorem (22) does not necessarily hold, nor is it true that the relation (21) is satisfied because usually numerical techniques diagonalize H_{el} only in a subspace of electronic wave functions. If we then reconsider the expression for E_1 , it turns out that the leading term is not A but that it is dominated by two other contributions A' of order $O(\kappa^1)$ and A'' of order $O(\kappa^2)$. Analogously, E_2 contains besides B of order $O(\kappa^2)$ two other terms B' of order $O(\kappa^1)$ and B'' of order $O(\kappa^2)$. When the Hellmann–Feynman theorem holds, both A' and B' are zero. When H_{el} is diagonalized in the subspace invariant under D , i.e. $\langle D\varphi | H_{\text{el}} - U | \varphi \rangle = 0$, both A'' and B'' are zero. We conclude that to find the results obtained above for the exact electronic wave function with approximate numerical functions, one should have

$$\langle \nabla\varphi | H_{\text{el}} | \varphi \rangle = O(\kappa^5) \quad \langle D\varphi | H_{\text{el}} - U | \varphi \rangle = O(\kappa^3), \quad (28)$$

i.e. the Hellmann–Feynman theorem and the diagonalization of H_{el} should be satisfied precisely enough, for all \mathbf{R} , so as to make A', A'' and B', B'' negligible compared to A and B , respectively.

3.3. NON-ADIABATIC VIBRATIONAL AND ROTATIONAL EFFECTS

So far, we have not distinguished between overall motion (translations and rotations) and internal vibrations. This distinction is important in a Born–Oppenheimer analysis since degrees of freedom associated with overall motion are not confined to the vicinity of the equilibrium configuration and can therefore not be subjected to Taylor expansion. In order to study the problem in detail, one must transform from the Cartesian coordinates \mathbf{R} and \mathbf{S} used earlier, to new coordinates which involve the nuclear centre-of-mass, the Eulerian angles and $3N - 6$ internal variables denoted by \mathbf{q} . Referring all particle positions to the nuclear centre-of-mass, one can always separate off the overall translation of the system. It should be mentioned that measuring the electronic positions from the nuclear centre-of-mass avoids the appearance of mixed nuclear and electronic gradients but generates so-called mass-polarization terms, mixed gradients of different electrons, which must be absorbed in the definition of the electronic Hamiltonian. From now on, the electronic wave functions refer to eigenstates of the electronic Hamiltonian involving mass-polarization terms.

In order to rewrite the quantities derived in the previous sections in terms of the new coordinates, we need the following expression of the nuclear gradient (neglecting the translational contribution):

$$\nabla_{\mathbf{R}} = \mathcal{K}\mathbf{J} + (1/\kappa)\mathcal{L}\nabla_{\mathbf{q}}, \quad (29)$$

where \mathcal{K} and \mathcal{L} are matrices depending on the internal variables \mathbf{q} only [11] and \mathbf{J} is the total nuclear angular momentum. The first term on the r.h.s. of (29) corresponds to the rotational motion of the nuclear frame and the second term to the vibrational motion. Note that the former does not contain the factor $1/\kappa$ in accordance with the

non-local nature of the rotation. In the spirit of the Born–Oppenheimer approximation, we will replace \mathcal{K} and \mathcal{L} by their value at equilibrium and choose for the variables \mathbf{q} the normal coordinates, i.e. those in which the quadratic part of the electronic potential energy surface $U^{(2)}$ is diagonal.

Under these approximations, the adiabatic Hamiltonian takes the form:

$$H^A = H^V + H^R + H^{VR}, \quad (30)$$

where

$$H^V = (\kappa^2/2) \sum_{r=1}^{3N-6} [-\Delta(q_r) + \omega_r^2 q_r^2],$$

$$H^R = (\kappa^4/2) \sum_{a=1}^3 \sum_{b=1}^3 J_a \mu_{ab} J_b,$$

where ω_r are the normal vibrational frequencies, whereas μ_{ab} is the inverse moment-of-inertia tensor at equilibrium. The term H^{VR} is the rotation–vibration coupling and can be minimized by a suitable choice of axes. In the case of small amplitude normal vibrations, this is done through the "Eckart conditions" [12]. The inertia tensor is then given by the classical expression.

Neglecting the rotation–vibration coupling, the adiabatic energy can be written as

$$E^A(v_r, J) = E_0 + \kappa^2 \sum_r (v_r + \frac{1}{2}) \omega_r + \kappa^4 E_i^J, \quad (31)$$

where E_i^J are the eigenvalues of the rotational secular equation, J is the rotational quantum number and v_r are the vibrational quantum numbers.

Introducing the above approximations for the Cartesian gradients and the form of the adiabatic nuclear wave function in expressions (23) and (24) for A and B , one discovers that these quantities can in turn be separated into vibrational and rotational parts. It also turns out that the non-adiabatic energy corrections E_1 and E_2 have the same form as the adiabatic terms. The vibrational part is linear in the vibrational quantum numbers and can hence be accounted for by changing the normal frequencies. The rotational part is quadratic in J and can be incorporated by adapting the moment-of-inertia tensor. For diatomic molecules, the analytic calculation can be performed more explicitly, we obtain for the non-adiabatic energy correction

$$\Delta E = \kappa^6 (v_r + \frac{1}{2}) \Delta \omega + O(\kappa^8), \quad (32)$$

with

$$\Delta \omega = -\omega \frac{\langle \nabla \varphi^{(1)} | \nabla \varphi^{(1)} \rangle^2}{\langle \nabla \varphi^{(1)} | H_{el} - U^{(0)} | \nabla \varphi^{(1)} \rangle}. \quad (33)$$

It follows from this expression that, for the electronic ground state, the correction $\Delta \varphi$ is negative.

3.4. SUMMARY

In this section, we have demonstrated that a perturbation analysis provides a qualitative understanding of the way in which the GCA describes non-adiabatic effects. We have shown that the GCA yields non-adiabatic energy corrections with the right sign (energy lowering) and of the right size (κ^6). Aside from the strictly mathematical perturbation procedure based on exact electronic wave functions, we have also studied the consequences of using approximate electronic states in numerical applications. This reveals the importance of certain properties of the electronic matrix elements, such as the Hellmann–Feynman theorem, to be valid sufficiently accurately. We have also shown that the non-adiabatic effects can be separated in vibrational and rotational contributions and how they depend on the corresponding quantum numbers.

4. The GCA for the hydrogen molecular ion

Any general approximation scheme for molecular systems should be tested by applying it to the simplest molecule: the hydrogen molecular ion H_2^+ . All traditional approaches have been worked out for this system [13]. As a test case, H_2^+ is unique in the sense that the exact electronic eigenstates are available if one solves the electronic Schrödinger equation in elliptical coordinates [14]. However, in applying the GCA [15, 16] we have chosen not to use this simplifying aspect pertaining to H_2^+ . On the one hand, one is almost forced not to use the exact electronic state in the GCA since a combination with a convolution function, even if expressed in elliptical coordinates, leads to unmanageable multicentre integrals. On the other hand, the use of an admittedly non-exact but yet accurate electronic state, built from Gaussian orbitals, puts a GCA application to H_2^+ on equal footing, as far as methodology is concerned, with similar calculations for larger diatomic systems.

4.1. COMPUTATIONAL STRATEGY

In the perturbation analysis of section 3, we have not explicitly taken into account the rotational invariance of the full molecular Hamiltonian. Here, however, we are after the calculation of vibration–rotation energies $E(v, J)$ labelled by a vibrational v and a rotational J quantum number. The latter specifies the total angular momentum value of the molecular system, i.e. the irreducible representation of the rotation group according to which the wave function transforms upon rotation.

In order to obtain the rotation–vibration energies and corresponding wave functions in the GCA, one has to carry out a four-stage procedure:

- (1) an electronic structure calculation over the range of internuclear distances accessible to nuclear vibrations;
- (2) the evaluation of overlap and Hamiltonian kernels between intrinsic states, i.e. products of electronic wave functions and nuclear convolution functions;

- (3) angular momentum projection, i.e. integration of the above-mentioned kernels with irreducible representations of the rotation group;
- (4) solution of the projected Wheeler equation, i.e. the Wheeler equation with the angular momentum projected kernels obtained in the previous stage.

Let us discuss some aspects of each of these steps in order to obtain an idea of the effort involved in obtaining GCA vibration–rotation levels.

As already stated above, we did not want to set up the calculations in such a way that they are fundamentally restricted to H_2^+ or even to diatomic molecules. We therefore did not use elliptical coordinates nor Slater orbitals, but expressed the electronic ground state of H_2^+ as a superposition of floating 1s Gaussian orbitals. Although it is possible, using enough basis functions, to produce a very accurate potential energy curve, GCA perturbation theory (see section 2) warns against contributions to the GCA energies arising from deficiencies in the associated electronic state. More specifically, we already know that the Hellmann–Feynman theorem should be satisfied. Another means of improving the quality of the electronic wave function is to impose the Virial theorem. For this purpose, a scaling method can be used, as demonstrated by Löwdin [17]. A parameter optimization developed by Hurley [18] can take care of the Hellmann–Feynman theorem. Since both these procedures are numerical, these theorems are satisfied to within a certain accuracy. The consequences of this are discussed below.

As a result of the above procedures, we obtained an approximate electronic ground state curve for H_2^+ which has a ± 3 digit accuracy when compared with Kolos' exact results [13].

Combining the electronic state, constructed with 1s Gaussians, with the choice

$$\phi = \exp[-(\mathbf{R} - S)^2/2W^2], \quad (34)$$

where \mathbf{R} is the vector joining the two protons, for the nuclear convolution function, allows us to calculate the GCA kernels using multicentre integrals for Gaussian orbitals. Unprojected kernels Δ and \mathcal{H} are then integrated with Legendre polynomials P^J to generate angular momentum projected versions Δ^J and \mathcal{H}^J according to the formulae

$$\Delta^J(S, S' | W) = \int_{-1}^1 P^J(\cos \theta) \Delta(S, S', \theta | W) d(\cos \theta), \quad (35)$$

$$\mathcal{H}^J(S, S' | W) = \int_{-1}^1 P^J(\cos \theta) \mathcal{H}(S, S', \theta | W) d(\cos \theta), \quad (36)$$

where the unprojected kernels appearing in the integrand are given by

$$\Delta(S, S', \theta | W) = \langle \chi(S \mathbf{e}_z, W) | \chi(S' \cos \theta \mathbf{e}_z + S' \sin \theta \mathbf{e}_x, W) \rangle, \quad (37)$$

$$\mathcal{H}(S, S', \theta | W) = \langle \chi(S e_z, W) | H | \chi(S' \cos \theta e_z + S' \sin \theta e_x, W) \rangle, \quad (38)$$

$$\chi(r, R | S, W) = \varphi(r | S) \phi(R | S, W), \quad (39)$$

where χ is the diatomic intrinsic state. These formulae apply for Σ states only. In the case of non-zero electronic angular momentum about the z -axis, Wigner d -functions [19] should replace the Legendre polynomials. The integrals over $\cos \theta$ can be performed analytically for the overlap kernel and the kinetic energy parts of the Hamiltonian kernel. Because of the appearance of incomplete gamma functions [20], this is not possible for the potential energy contributions. However, we expect the relevant W -values to be quite small, which implies that the integrands in (35) are appreciably different from zero if $\cos \theta \equiv 1$. One can therefore expand the unprojected kernels in a Taylor series in $\cos \theta$ such that a term-by-term integration yields a rapidly converging series in W for the projected kernels. Comparing this procedure with numerical integration proved to be the faster method.

Having performed steps 2 and 3, one needs to solve the Wheeler integral equation associated with the kernels (35) in order to obtain the GCA energies as a function of the width parameter W . For a fixed J , we expect to find a quasi-harmonic oscillator spectrum. The associated weight functions, for small enough values of W , should hence not differ too much from oscillator eigenstates. It is therefore a good strategy to set up the Wheeler equation in a harmonic oscillator basis with the oscillator frequency of the potential energy curve. This leads us to a generalized eigenvalue problem containing the two matrices given by

$$\Delta_{mn}^J(W) = \int \int F_m^0(S) \Delta^J(S, S' | W) F_n^0(S') dS dS', \quad (40)$$

$$\mathcal{H}_{mn}^J(W) = \int \int F_m^0(S) \mathcal{H}^J(S, S' | W) F_n^0(S') dS dS'. \quad (41)$$

These two-dimensional integrals have to be performed numerically. We found it to be advantageous to discretize along the $S + S'$ and $S - S'$ directions. This is due to the fact that in the $S + S'$ direction, the Hamiltonian kernel strongly resembles the electronic potential energy curve, while in the $S - S'$ direction, one finds a quadratic behaviour typical for a generator coordinate representation of kinetic energy operators. In order to obtain energy eigenvalues of sufficient accuracy to detect non-adiabatic effects, the integrations in (40) and (41) have to be done very carefully. Typically, we found that it requires ± 1000 kernel evaluations on a fixed mesh to obtain for every $J = 1, 2, 3, \dots$ the GCA vibrational energies to an accuracy of 8 digits at each given value of W .

4.2. GROUND STATE ENERGY

The GCA approximation to the ground state energy of H_2^+ is the lowest eigenvalue of the Wheeler equation with the projected kernels (35) for $J = 0$. Since the latter

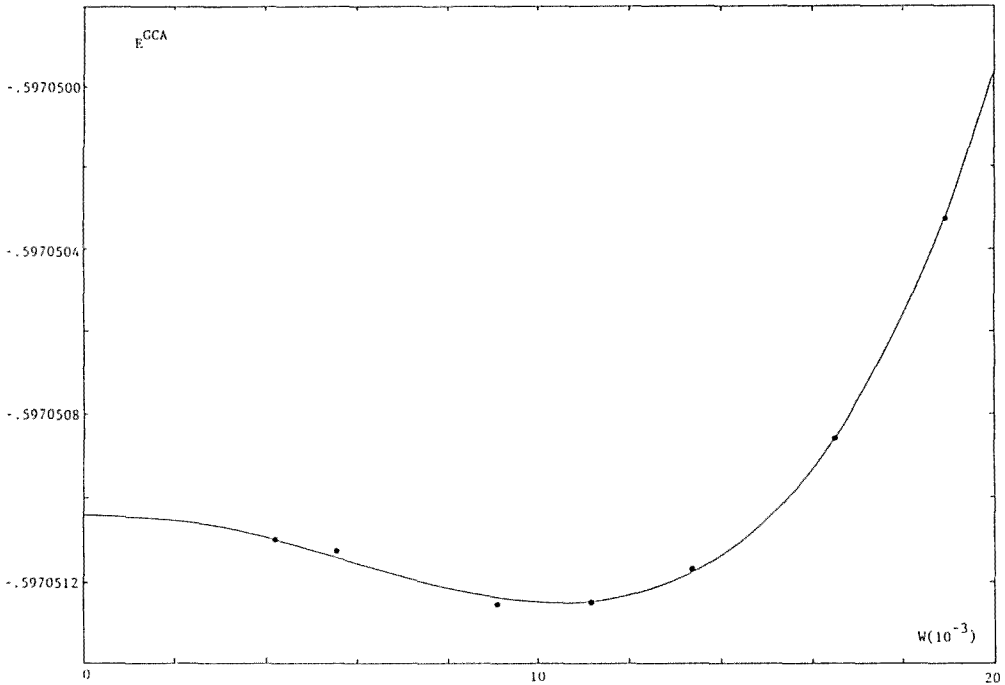


Fig. 1. Least-squares two-term polynomial fit of the GCA ground state energy as a function of W . The dots represent the computed data points.

quantities are W -dependent, so are the eigenvalues. Following the variational method, we calculated the energy for different values of W and minimized. This was achieved by proposing a two-term polynomial fit, shown in fig. 1,

$$E(W) = E(0) + aW^2 + bW^4. \quad (42)$$

We prefer to use the width parameter W , rather than the parameter ε in numerical applications. We obtained the following values* for the coefficients:

$$E(0) = -0.59705106, \quad (43)$$

$$a = -0.037014, \quad (44)$$

$$b = +16.027. \quad (45)$$

This yields a GCA ground state energy at $W_0 = 0.010746$, with

$$E^{GCA} = E(W_0) = -0.59705126. \quad (46)$$

*In this paper, all numerical values are given in atomic units.

This value should now be compared with the adiabatic ground state energy which was calculated separately using the potential energy curve and the associated adiabatic correction term. As predicted by the theory, we find that the ground adiabatic state indeed coincides with the limit as $W \rightarrow 0$ of the GCA energies $E(W)$, i.e.

$$E^A \equiv E(0) = -0.59705106. \quad (47)$$

We can therefore conclude that the GCA ground state energy is lower than the adiabatic one. The magnitude of the non-adiabatic correction introduced by the GCA in this case is:

$$\Delta E = E^{\text{GCA}} - E^A = -2.0 \times 10^{-7}, \quad (48)$$

which is indeed $O(\kappa^6)$ as predicted by general theory. This energy gain represents $\cong 40$ percent of the full non-adiabatic effect as calculated by Kolos using the coupled differential equations approach. Since we used overall scaling and parameter optimization to satisfy the Virial and Hellmann–Feynman theorems, the remaining non-adiabatic effect of $O(\kappa^6)$ must be attributed to the inaccuracy of the electronic state used in the GCA procedure.

4.3. EXCITED STATES

The rotationless vibrationally excited states are obtained as the successive eigenvalues of the Wheeler equation with $J = 0$. The rotationally excited states with total angular momentum J are calculated from Wheeler equations containing kernels obtained from (35) and (36) with this J value. From the ground state calculation, we know that the three-term formula of type (42) accurately fits the GCA energies. Therefore, calculations for three fixed W values were made, from which the coefficients $E(0)$, a and b were obtained. Table 1 lists these quantities for $J = 0, 1, 2, 3$ and $v = 0, 1, 2, 3$, while in table 2 we list the corresponding GCA energies at the optimum values W_0 and the non-adiabatic effects at these values. We also list the non-adiabatic effects for all vibrational states at the value of W that minimizes the vibrational ground state for each J . The reason is that it is in principle not allowed to separately minimize w.r.t. W the various vibrational energies for the same J , since the resulting wave functions would not be orthogonal. Evidently, in order to maintain orthogonality, one loses a fraction of the energy lowering. Observe that there is an increase in the optimum W_0 values and of the non-adiabatic effect with increasing v . This is consistent from the physical point of view: larger non-adiabatic effects are evidence of stronger coupling between electronic and nuclear motion, and this is reflected in larger values of the width parameter.

In order to study the behaviour of the GCA non-adiabatic corrections $\Delta E(v, J) = E^{\text{GCA}}(v, J) - E^A(v, J)$ as a function of the vibrational and rotational quantum numbers v and J , we first recall the simplest fit to the adiabatic spectrum

Table 1

Eigenvalues of the Hill–Wheeler equation with $v = 0, 1, 2, 3$ at W equal to 0.0129, 0.0158 and 0.0190 for total angular momentum J equal to 0, 1, 2, 3

$J \setminus v$	0	1	2	3
0.0190				
0	-0.59705117	-0.58693535	-0.57733970	-0.56810926
1	-0.59678541	-0.58668256	-0.57709886	-0.56787557
2	-0.59625597	-0.58627897	-0.57661905	-0.56740952
3	-0.59546695	-0.58542851	-0.57590388	-0.56671371
0.0158				
0	-0.59705126	-0.58693532	-0.57733953	-0.56810895
1	-0.59678550	-0.58668253	-0.57709870	-0.56787525
2	-0.59625607	-0.58617894	-0.57661888	-0.56740920
3	-0.59546706	-0.58542848	-0.57590371	-0.56671338
0.0129				
0	-0.59705127	-0.58693522	-0.57733931	-0.56810861
1	-0.59678551	-0.58668243	-0.57709848	-0.56787491
2	-0.59625608	-0.58617885	-0.57661866	-0.56740886
3	-0.59546707	-0.58542839	-0.57590350	-0.56671302

Table 2

Optimum values W_0 , corresponding GCA energies E^{GCA} and non-adiabatic corrections ΔE . The ΔE_0 are the non-adiabatic corrections obtained for the single width parameter minimizing the ground state energy

$J \setminus v$	0	1	2	3
W_0				
0	0.009954	0.012946	0.015065	0.016724
1	0.009878	0.012921	0.015052	0.016770
2	0.009755	0.012858	0.015030	0.016834
3	0.009576	0.012767	0.015002	0.016947
E^{GCA}				
0	-0.59705128	-0.58693536	-0.57733975	-0.56810950
1	-0.59678552	-0.58668257	-0.57709892	-0.56787581
2	-0.59625609	-0.58617898	-0.57661910	-0.56740978
3	-0.59546708	-0.58542851	-0.57590393	-0.56671399
$\Delta E \times 10^{10}$				
0	-1590	-5246	-10818	-17938
1	-1535	-5197	-10805	-18091
2	-1471	-5126	-10780	-18415
3	-1381	-5027	-10762	-18992
$\Delta E_0 \times 10^{10}$				
0	-1589	-4393	-7432	-10534
1	-1534	-4361	-7433	-10578
2	-1467	-4326	-7432	-10703
3	-1370	-4276	-7439	-10923

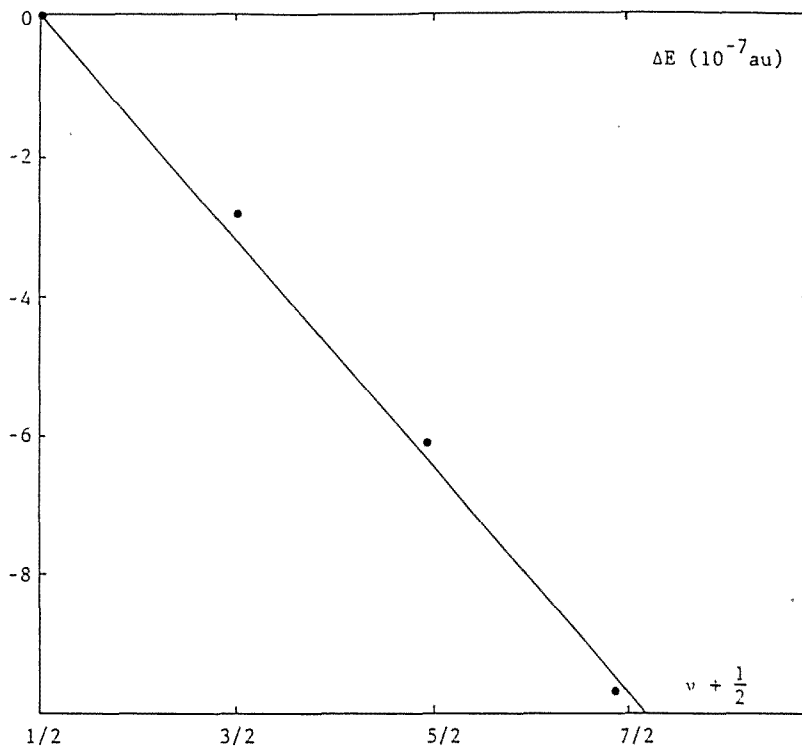


Fig. 2. The GCA non-adiabatic corrections at $W = 0.010$ versus vibrational quantum numbers for $J = 3$. The origin is chosen at $\Delta E(0, 3)$.

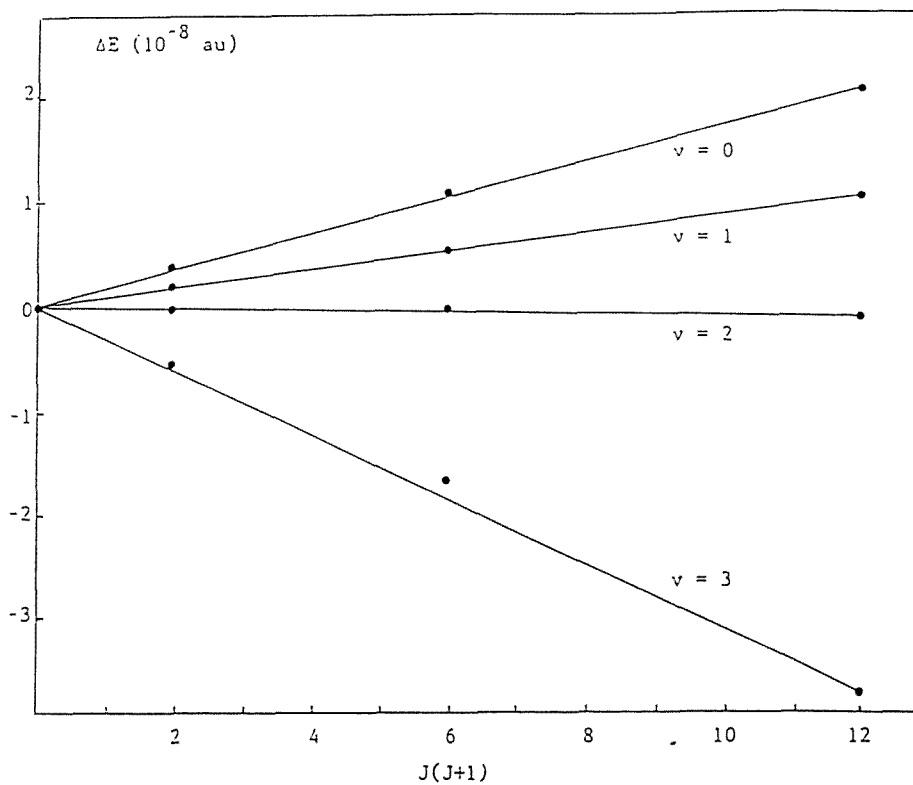


Fig. 3. The GCA non-adiabatic corrections at $W = 0.010$ versus rotational quantum numbers for $v = 0, 1, 2, 3$. The origin is chosen at $\Delta E(v, 0)$.

$$E^A(v, J) = E^A(0, 0) + \left(v + \frac{1}{2}\right) \omega^A + J(J+1)/2I^A, \quad (49)$$

where ω^A and I^A are the adiabatic frequency and moment of inertia. In view of the smallness of the non-adiabatic effects, we expect a similar formula to hold for the GCA, i.e.

$$E^{\text{GCA}}(v, J) = E^{\text{GCA}}(0, 0) + \left(v + \frac{1}{2}\right) \omega^{\text{GCA}} + J(J+1)/2I^{\text{GCA}}. \quad (50)$$

Putting $\Delta\omega = \omega^{\text{GCA}} - \omega^A$ and $\Delta I = I^{\text{GCA}} - I^A$, one easily finds that

$$\Delta E(v, J) = \left(v + \frac{1}{2}\right) \Delta\omega - J(J+1) \left[\Delta I/2 (I^A)^2 \right], \quad (51)$$

i.e. one expects a linear behaviour of the GCA correction as a function of the discrete variables $v + 1/2$ and $J(J \pm 1)$. Figures 2 and 3 confirm the above analysis. The reason behind the validity of the above simple relationship is that in both the adiabatic approximation and the GCA, the total energy can be expanded as a Dunham series (see next section). From table 3, we see that $\Delta\omega$ is negative and quasi-independent

Table 3

Harmonic frequency and moment of inertia corrections			
J	$\Delta\omega$ [cm ⁻¹]	v	$\Delta I/2(I^A)^2$ [MHz]
0	-0.0654	0	-12.10
1	-0.0662	1	-6.39
2	-0.0676	2	-0.34
3	-0.0699	3	+21.40

of J (we therefore show only the v -dependence for $J = 3$). This confirms the theoretical prediction (33). On the other hand, ΔI is strongly dependent on v ranging from negative to positive values. This v -dependence is due to anharmonicity, as will become clear in the next section.

4.4. SUMMARY

In this section, we have summarized the computational strategy and numerical results of a GCA calculation on H_2^+ using a realistic electronic state as input. The theoretical predictions of section 3 were confirmed, i.e. the GCA yields upper bounds to the exact energies that lie below the adiabatic ones. The non-adiabatic effects are of the right order of magnitude in spite of the use of a moderately accurate electronic wave function. However, this state should at least fulfill the Virial theorem and the Hellmann–Feynman theorem to sufficient accuracy.

5. Derivation of the GCA Dunham series

The gross features of diatomic spectra can be explained by a threefold partition of the molecular energy

$$E \cong E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}, \quad (52)$$

where E_{el} stands for the electronic energy, while E_{vib} and E_{rot} are the vibrational and rotational energy of the nuclei, respectively. Such a formula provides a zeroth order description of the energy level pattern. However, coupling terms between the various types of motion lead to correction terms such that a refinement of the energy expression is required. It was first demonstrated by Dunham [4], using semiclassical methods, and it can be readily shown in the adiabatic approximation that the total molecular energy can actually be written as a series expansion in $(v + 1/2)$ and $J(J + 1)$, i.e.

$$E(v, J) = \sum_{kl} Y_{kl} \left[v + \frac{1}{2} \right]^k [J(J + 1)]^l. \quad (53)$$

This formula is known as the Dunham series and provides an excellent phenomenological tool for the parametrization of diatomic spectra. The constants Y_{kl} are obtained by fitting spectral lines to differences of energy levels from (53). Therefore, if the GCA is to be an improved alternative to the adiabatic approximation, also from a phenomenological point of view, it should be possible to derive the Dunham series within the GCA formalism. It is the purpose of this section to sketch the derivation of (53) from the GCA integral equation [21].

5.1. SEPARATION OF MOLECULAR ENERGIES AND KERNEL EXPANSIONS

Our first task is to show that the GCA eigenvalues approximately partition as in (52). We therefore consider the overall topological features of the basic dynamical GCA quantities, i.e. the unprojected kernels, around the point $S = S' = S_0$ and $\theta = 0$. Here, S_0 is the value of the generator coordinate for which the GCA intrinsic energy $\mathcal{H}(S, S, 0)/\Delta(S, S, 0) = E(S)$ has a minimum. Up to a constant, $E(S)$ is approximately equal to the potential energy function in the adiabatic theory. Therefore, S_0 is very close to the equilibrium distance R_0 of the adiabatic approximation.

Due to the fact that the convolution function is a sharply localized Gaussian, it can be shown that the following expressions provide good approximations for the unprojected overlap and the ratio $\mathcal{K} = \mathcal{H}/\Delta$ around the reference configuration $S = S' = S_0$ and $\theta = 0$:

$$\Delta(S, S', \theta) \cong \exp[-s_V(S - S')^2] \exp[-s_R \theta^2] \equiv \Delta_V^0(S, S') \Delta_R^0(\theta), \quad (54)$$

$$\begin{aligned} \mathcal{K}(S, S', \theta) &\cong E(S_0) + \frac{1}{2} [B(S - S_0)^2 + 2A(S - S_0)(S' - S_0) + B(S' - S_0)^2] - \frac{1}{2} C \theta^2 \\ &\equiv E(S_0) + \mathcal{K}_V^0(S, S') + \mathcal{K}_R^0(\theta). \end{aligned} \quad (55)$$

These are termed the Gaussian overlap and quadratic approximations to the unprojected kernels. Explicit expressions for the parameters s_V and s_R and A, B, C^* can be given in terms of the Hamiltonian and the intrinsic states $\chi(S_0 e_2)$. In particular, if W is of order κ^2 it follows that s_V and s_R are of order $1/\kappa^4$ such that the Gaussian kernels in (54) are sharply peaked. If one now introduces (53) and (54) in the GCA energy expression, one readily obtains

$$E^{\text{GCA}} = E(S_0) + \frac{(F|\Delta_V^0 \mathcal{K}_V^0|F)}{(F|\Delta_V^0|F)} + \frac{\int_{-1}^1 d \cos \theta P_J(\cos \theta) \Delta_R^0 \mathcal{K}_R^0}{\int_{-1}^1 d \cos \theta P_J(\cos \theta) \Delta_R^0}, \quad (56)$$

where $(,)$ denote double radial integrations over S and S' . One can now identify $E(S_0)$ with the major part of the electronic energy, the second term depending only on the vibrational-like kernels \mathcal{K}_V^0 and Δ_V^0 , with the vibrational energy and the last term involving only the rotation angle θ with the rotational energy. Thus, the above formula explains the partitioning (52) starting from the GCA expression for the total energy.

Minimization of the second term in (56) with respect to the vibrational weight function F can be shown to lead to a harmonic oscillator spectrum. If, in view of the peaked structure of $\Delta_R^0(\theta)$, one replaces $P_J(\cos \theta)$ in the third term by its asymptotic expansion $1 - (1/4)J(J+1)\theta^2 + \dots$, the last term can be evaluated analytically. The end result is an energy formula of the type (50), namely

$$E^{\text{GCA}}(v, J) \equiv E(S_0) - A/4s_V - C/2s_R + (v + \frac{1}{2}) \omega^{\text{GCA}} + J(J+1)/2I^{\text{GCA}}, \quad (57)$$

where

$$\omega^{\text{GCA}} = (A^2 - B^2)^{1/2}/2s_V, \quad I^{\text{GCA}} = 4s_R^2/C. \quad (58)$$

Here, the GCA vibrational frequency and moment of inertia are given explicitly in terms of the parameters of the Gaussian overlap and quadratic approximations. Aside from the GCA frequency ω^{GCA} , it is also possible to define a GCA mass parameter by rewriting \mathcal{K}_V^0 in terms of the variables

$$D = S - S', \quad G = (S + S')/2 - S_0, \quad (59)$$

to obtain

$$\mathcal{K}_V^0 = (-2s_V/M^{\text{GCA}}) D^2 + \left[M^{\text{GCA}} (\omega^{\text{GCA}})^2 / 2 \right] G^2, \quad (60)$$

with $M^{\text{GCA}} = 8s_V^2/(A - B)$. Griffin and Wheeler [22] showed that, if multiplied with Δ_V^0 , the D^2 acts as a kinetic energy operator $(2M^{\text{GCA}})^{-1} d^2/dS^2$, while the G^2 term

*There should be no confusion with the symbols A and B used in section 3.

corresponds to an oscillator potential. Thus, the Wheeler equation corresponding to the zeroth order vibrational kernels is equivalent to a harmonic oscillator with the above defined GCA mass and frequency.

In the adiabatic approximation, one succeeds in going beyond the zeroth order vibration–rotation picture provided by the first three terms of (53), by expanding the potential energy function beyond the second order and treating the higher order terms by perturbation theory. In the GCA, one can accomplish the same goal by pushing the kernel expansions to higher orders. More precisely, since the functions $\log \Delta(S, S', \theta)$ and $\mathcal{K}(S, S', \theta)$ are smooth functions of their arguments, one expands

$$\log \Delta = \sum_{klm} \Delta_{klm} \frac{(S - S_0)^k}{k!} \frac{(S' - S_0)^l}{l!} \frac{\theta^{2m}}{2m!}, \tag{61}$$

$$\mathcal{K} = \sum_{klm} \mathcal{K}_{klm} \frac{(S - S_0)^k}{k!} \frac{(S' - S_0)^l}{l!} \frac{\theta^{2m}}{2m!}. \tag{62}$$

Only even powers of θ appear due to time reversal invariance. Explicit expressions for the expansion coefficients are given in [21]. Truncation at second order yields the zeroth order picture of the previous paragraph. Higher order truncation is not directly suitable for a perturbation theory treatment because the above functions do not appear directly in the Wheeler equation. However, one can recast the above expansions in the forms

$$\Delta = \Delta_V^0 \Delta_R^0 [1 + \mathcal{W}], \tag{63}$$

$$\mathcal{H} = \Delta_V^0 \Delta_R^0 [\mathcal{K}_V^0 + \mathcal{L}], \tag{64}$$

where, if the Gaussian overlap and quadratic approximations are already accurate, the kernels \mathcal{W} and \mathcal{L} are such that $|\mathcal{W}| \ll 1$ and $|\mathcal{L}| \ll |\mathcal{K}_V^0|$. In order to use the equivalence of the second order Wheeler equation with the harmonic oscillator differential equation, it is also advantageous to write the expansion of \mathcal{W} and \mathcal{L} in terms of the variables D and G

$$\mathcal{W} = \sum_{pqm} \mathcal{W}_{pqm} G^p D^{2q} \theta^{2m}, \tag{65}$$

$$\mathcal{L} = \sum_{pqm} \mathcal{L}_{pqm} G^p D^{2q} \theta^{2m}, \tag{66}$$

where $p + 2q > 2$ and only even powers in D occur due to hermiticity of the Wheeler kernels. These terms constitute the corrections to the lowest order picture of a harmonic oscillator plus rigid rotor, and can be catalogued as pure D, G terms describing anharmonicities, pure θ terms describing centrifugal distortion and mixed terms, describing rotation–vibration couplings.

5.2. ANGULAR MOMENTUM PROJECTION AND VIBRATIONAL PERTURBATION THEORY

Angular momentum projection amounts to the integration of the unprojected kernels with a Legendre polynomial (see (35) and (36)). In this process, the following quantities, termed rotational moments, appear

$$R_m(J) = \frac{\int_{-1}^1 d \cos \theta P_J(\cos \theta) \Delta_R^0(\theta) \theta^{2m}}{\int_{-1}^1 d \cos \theta P_J(\cos \theta) \Delta_R^0(\theta)}. \quad (67)$$

If expressed in terms of θ -powers, the P_J have coefficients that are polynomials in $J(J+1)$:

$$P_J(\cos \theta) = \sum_{n=0}^{\infty} P_n(J) \theta^{2n}, \quad (68)$$

$$P_n(J) = \sum_{l=0}^n P_n^l [J(J+1)]^l, \quad (69)$$

with constants P_n^l that may be tabulated [21]. The rotational moments, after expressing the ratio of two series as one, then take the form

$$R_m(J) = (1/s_R)^m \sum_{l=0}^{\infty} R_m^l [J(J+1)]^l, \quad (70)$$

with R_m^l derived explicitly in [21]. This is a crucial step toward establishing the Dunham series since it involves precisely the $J(J+1)$ powers. Using the above properties, one obtains the projected kernels in the form

$$\Delta^J = \Delta_V^0 [1 + \mathcal{W}^J], \quad (71)$$

$$\mathcal{H}^J = \Delta_V^0 [E(S_0) + \mathcal{X}_V^0 - 2R_1(J) s_R^2 / I^{\text{GCA}} + \mathcal{L}^J], \quad (72)$$

where now we have introduced angular momentum projected perturbations \mathcal{W}^J and \mathcal{L}^J which are functions of D and G only and which no longer depend on θ . They can be written in the form

$$\mathcal{W}^J = \sum_{pq} \mathcal{W}_{pq}^l [J(J+1)]^l G^p D^{2q}, \quad (73)$$

$$\mathcal{L}^J = \sum_{pq} \mathcal{L}_{pq}^l [J(J+1)]^l G^p D^{2q}. \quad (74)$$

The projected Wheeler equation has thus acquired a form suitable for (double) perturbation theory. Starting from the zeroth order problem which we know to be equivalent with a harmonic oscillator problem, we can express the higher order energy corrections in the perturbation expansion in terms of basic integrals containing powers of D and G and oscillator eigenfunctions. It is well known that such integrals can be expressed in powers of $v + 1/2$. Therefore, by regrouping contributions of different order energy corrections to specific powers of $J(J + 1)$ and $v + 1/2$, one can ultimately put the GCA energy in the form

$$\begin{aligned} E^{\text{GCA}}(v, J) &= E^0(v, J) + E^1(v, J) + E^2(v, J) + \dots \\ &= \sum_{kl} Y_{kl}^{\text{GCA}} \left[v + \frac{1}{2} \right]^k [J(J + 1)]^l. \end{aligned} \quad (75)$$

The spectroscopic constants Y_{kl}^{GCA} are unique functions of the kernel parameters s_V, s_R (Gaussian overlap widths), $M^{\text{GCA}}, \omega^{\text{GCA}}, I^{\text{GCA}}$ (mass, frequency and inertia of the GCA vib-rotor spectrum) and the coefficients L_{pqm} and W'_{pqm} . The explicit derivation of the Y_{kl} in terms of these is a complex procedure. This is due to the fact that in the GCA we have to deal with two kernels containing three variables, instead of the expansion of a single function (the potential energy curve) of one variable in the adiabatic approximation.

5.3. SUMMARY

We have shown that a zeroth order approximation to diatomic Wheeler kernels yields the crude partitioning of the total molecular energy in electronic, vibrational and rotational parts. A subsequent treatment of the remainder by order-by-order angular momentum projection and double perturbation theory makes it possible to establish a derivation of the Dunham series within the framework of the GCA. The merit of the above derivation is that, in view of the higher intrinsic accuracy of the GCA, the Dunham series justifies the parametrization of diatomic spectra to within errors of order κ^8 . However, this information should then be stored in the overlap and Hamiltonian kernel coefficients rather than in potential energy coefficients. A procedure for how to identify non-adiabatic effects in such fits has been outlined in [21].

6. GCA for curve-crossing problems

In the previous sections we have shown, both theoretically and numerically, that the GCA is an approximation scheme superior to the traditional adiabatic approximation. However, we limited ourselves to energy levels near potential energy minima, thus excluding the important case of (near) electronic degeneracies. In this paper, we consider applications to diatomic systems only, which means that we

should now focus on so-called “curve crossing” situations, i.e. energy ranges in which there is a (near) degeneracy between electronic potential energy curves. It is well known that the non-adiabatic effect on energy levels in these crossing regions is orders of magnitude larger than near potential energy minima [23]. This is due to large coupling matrix elements between the two electronic states involved. In order to study the performance of the adiabatic and GC approximations under these conditions [24], we have considered a model Hamiltonian which, after the formal separation of electronic and nuclear motion, simulates well the realistic two-state curve-crossing situation.

6.1. TWO-STATE MODELS

We consider the following Hamiltonian:

$$H = (T + V)\sigma_0 + \zeta\sigma_z + \xi\sigma_x, \quad (76)$$

where V , ζ and ξ are functions of a nuclear coordinate R and T is the kinetic energy operator $-(2\mu)^{-1}(d^2/dR^2)$. In (76), σ_0 is the 2×2 unit matrix, while σ_z and σ_x are Pauli spin matrices so that

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (77)$$

are the σ_z eigenstates with eigenvalues ± 1 , respectively. Model Hamiltonians of the above type have been studied extensively in molecular physics, solid state physics and statistical mechanics ([25, 26] and references therein). For our purposes, let us first consider the electronic problem arising from (76) if we omit the nuclear kinetic energy in view of the large value of the diatomic reduced mass μ , i.e.

$$(V\sigma_0 + \zeta\sigma_z + \xi\sigma_x)|\varphi_n\rangle = U_n|\varphi_n\rangle, \quad (78)$$

or in matrix notation

$$\begin{pmatrix} V_+ & \xi \\ \xi & V_- \end{pmatrix} \begin{pmatrix} c_n^+ \\ c_n^- \end{pmatrix} = U_n \begin{pmatrix} c_n^+ \\ c_n^- \end{pmatrix}, \quad (79)$$

where $V_{\pm} = V \pm \zeta$. This electronic Schrödinger equation represents two states V_{\pm} interacting via the coupling function ξ . The electronic eigenstates of (78) are linear combinations of the σ_z eigenfunctions and the associated eigenvalues can readily be computed by diagonalization of (80). We obtain

$$U_{1,2} = V \mp (\zeta^2 + \xi^2)^{1/2}, \quad (80)$$

$$|\varphi_n\rangle = c_n^+|+\rangle + c_n^-|-\rangle, \quad (81)$$

with $n = 1, 2$. One can now define a "crossing region" as the neighbourhood of the point where ζ vanishes, i.e. for which the potential energy curves would cross in the absence of coupling. Let us denote this point by R_c such that $\zeta(R_c) = 0$. If one assumes that at large distances from R_c the coupling function ξ goes to zero more rapidly than the difference potential $\zeta = (V_+ - V_-)/2$, one can show that the electronic eigenstates tend to pure spin states $|\pm\rangle$ as $R \rightarrow \pm\infty$ (in the present version of the model, the radial variable R is assumed to run from $-\infty$ to $+\infty$, but this will not affect the conclusions).

Since at all R distances both the spin states $|\pm\rangle$ and the Born–Oppenheimer electronic states $|\varphi_{1,2}\rangle$ span the electronic part of the space on which H is defined, we can write the exact solutions to the Schrödinger equation for H in two alternative forms:

$$F_1(R)|\varphi_1\rangle + F_2(R)|\varphi_2\rangle \tag{82}$$

or

$$D_+(R)|+\rangle + D_-(R)|-\rangle. \tag{83}$$

The respective nuclear factors $F_{1,2}(R)$ and $D_{\pm}(R)$ need to satisfy the coupled second order differential equations

$$\begin{pmatrix} T + U_1 + \Delta U_1 & U_{12} \\ U_{21} & T + U_2 + \Delta U_2 \end{pmatrix} \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} = E \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} \tag{84}$$

or

$$\begin{pmatrix} T + V_+ & \xi \\ \xi & T + V_- \end{pmatrix} \begin{pmatrix} D_+ \\ D_- \end{pmatrix} = E \begin{pmatrix} D_+ \\ D_- \end{pmatrix}. \tag{85}$$

The set of equations (84) are known as the adiabatic coupled equations. They contain the potentials $U_{1,2}$, which have an avoided crossing at R_c , modified by the so-called adiabatic corrections $\Delta U_{1,2}$ which in the present case are given by

$$\Delta U_1 = \Delta U_2 = \frac{1}{8\mu} \left(\frac{1}{1 + \rho^2} \right)^2 \left(\frac{d\rho}{dR} \right)^2, \tag{86}$$

with $\rho = \zeta/\xi$. These potentials interact via the coupling operators U_{12} and U_{21} , which depend of R and d/dR and are given explicitly in [24]. Equations (85), on the other hand, are known as the diabatic set of coupled equations. They contain the two intersecting potentials V_+ and V_- interacting via a smooth coupling function $\xi(R)$. The standard way of obtaining the diabatic representation from the adiabatic one is to require that the momentum coupling term $\langle\varphi_1|d/dR|\varphi_2\rangle$ vanishes [27]. Here it is clear that, since the pure spin states $|\pm\rangle$ are R independent, they satisfy this requirement. In realistic cases, one finds that the adiabatic corrections and couplings are large and sharply peaked around R_c , whereas the diabatic coupling function is small and slowly

varying through the crossing region. It is therefore advantageous to generate accurate numerical solutions to the Schrödinger equation for H via the diabatic coupled equations. We shall do so in the numerical applications.

6.2. WEAK AND STRONG ADIABATIC COUPLING LIMITS

The two-state model presented here is ideally suited to test the accuracy of approximation schemes that extract information from an electronic state to produce molecular energies and properties. Indeed, the electronic eigenstates are known analytically such that any errors left are due purely to the approximation scheme in question.

Before discussing the actual calculations at the various stages of approximation, it is instructive to consider two limiting forms of the Hamiltonian obtained by putting either the difference potential ζ or the coupling function ξ equal to zero.

In the limit $\xi = 0$, the electronic potentials are simply

$$U_1 = V - \xi, \quad U_2 = V + \xi. \quad (87)$$

Since realistically ξ is positive and almost constant, U_1 and U_2 do not cross. Actually, in the extreme case of constant ξ the potential curves are parallelly displaced with respect to each other. The associated electronic states in this limit are $|+\rangle \pm |-\rangle$, i.e. independent of R , which implies that the adiabatic correction terms and couplings vanish. Therefore, eqs. (84) decouple and the adiabatic approximation becomes exact. Also, since the trial space includes the adiabatic wave function for zero width, it will equally yield the exact solution in the limit $\zeta = 0$. If $\zeta \equiv 0$, we expect a weak coupling in (84) and we therefore term the limit $\zeta = 0$ the "weak adiabatic coupling limit".

Consider now the other limiting case $\xi = 0$. The electronic eigenvalues are now

$$U_1 = V - |\zeta|, \quad U_2 = V + |\zeta| \quad (88)$$

(per definition, 1 is the lower and 2 the upper curve). Since at R_c we have $\zeta(R_c) = 0$, there is now a true electronic degeneracy at R_c . One can show [24] that the electronic eigenstates in this limit have spinor components

$$c_1^+ = h - 1, \quad c_1^- = h, \quad c_2^+ = h, \quad c_2^- = 1 - h, \quad (89)$$

where h is the Heaviside step function $h(R - R_c)$, i.e. $h(x) = 0$ for $x < 0$ and $h(x) = 1$ for $x > 0$. It is clear that if $\xi = 0$, we have decoupling of the diabatic coupled equations (85) and hence the diabatic states $D_+(R) |+\rangle$ and $D_-(R) |-\rangle$ are the exact solutions if D_\pm are the eigenfunctions of the equations

$$(T + V \pm \zeta)D_\pm = E_\pm D_\pm. \quad (90)$$

The vanishing of the diabatic coupling function implies the divergence of the adiabatic correction term and the adiabatic coupling operator. The nature of these singularities

becomes clear if we assume that around R_c the function ξ is constant, while ζ can be approximated linearly with slope λ . The correction term now becomes the square of a Lorentzian

$$\frac{\xi^2}{8m} \left[\frac{\lambda}{(R - R_c)^2 + (\xi/\lambda)^2} \right]^2. \tag{91}$$

Clearly, the area under the potential energy barrier created by the adiabatic correction term tends to infinity as ξ goes to zero. Therefore, the divergence at the crossing point is stronger than a Dirac delta function potential. An actual wall is erected at $R = R_c$ looking from either side of the crossing point. This divergency is the mathematical signature of the so-called "breakdown of the adiabatic approximation". Indeed, even if one neglects the coupling operators, the adiabatic eigenvalues must be obtained from Schrödinger equations with truncated potentials

$$V - |\zeta| \text{ if } R > \text{ or } < R_c \text{ and } +\infty \text{ if } R \leq \text{ or } \geq R_c, \tag{92}$$

$$V + |\zeta| \text{ if } R > \text{ or } < R_c \text{ and } +\infty \text{ if } R \leq \text{ or } \geq R_c, \tag{93}$$

since per definition the electronic eigenvalue 1 is the lower and 2 the upper potential energy curve. The eigenfunctions of these potentials must vanish at $R = R_c$ and are zero on either of the half lines $R \geq R_c$ or $R \leq R_c$. Therefore, they never coincide with the exact solutions and there is always a finite non-adiabatic effect in the limit $x \rightarrow 0$. In view of the behaviour of the adiabatic approximation in this limiting case, we will refer to the limit $\xi \rightarrow 0$ as the strong adiabatic coupling limit.

Turning to the GCA, it is then logical to ask the question: how does the GCA behave in the strong adiabatic coupling limit? In order to answer this question, we observe that due to the special form of the electronic states as ξ goes to zero, the GCA integral in this limit divides into two terms:

$$|+\rangle \int_{-\infty}^{R_c} F(S)\Phi(R|S, W)dS + |-\rangle \int_{R_c}^{+\infty} F(S)\Phi(R|S, W)dS. \tag{94}$$

A theorem on coherent states by Bargmann et al. [28] implies that any infinite set of Gaussians labelled by centres that converge to a finite limit constitutes a complete set for square integrable functions on the real line. Clearly, the Gaussians centered on either of the half lines $]-\infty, R_c]$ and $[R_c, +\infty[$ both include complete sets for square integrable functions such that $F(S)$ restricted to the above intervals can always be chosen to represent $D_-(R)$ and $D_+(R)$, respectively,

$$D_+(R) = \int_{-\infty}^{R_c} F(S) \exp\left(-\frac{(R - S)^2}{2W^2}\right) dS, \tag{95}$$

$$D_-(R) = \int_{R_c}^{+\infty} F(S) \exp\left(-\frac{(R - S)^2}{2W^2}\right) dS. \tag{96}$$

Therefore, the GCA states can be made to coincide with the true eigenstates, i.e. the GCA becomes exact in the strong adiabatic coupling limit.

6.3. NUMERICAL RESULTS

In order to compare the adiabatic approximation and the GCA on realistic curve crossing situations and to numerically verify the theoretical findings in the strong coupling limit, we construct a model Hamiltonian for the EF , $GK^1\Sigma_g^+$ potentials of hydrogen [29] and the b' , $c'^1\Sigma_u^+$ potentials of nitrogen [30], respectively. In order to model the curve crossing situations in these diatomic molecules, we took the simplest possible representation for the diabatic states, i.e. quadratic expressions

$$V_{\pm}(R) = \frac{1}{2} k_{\pm}(R - R_{\pm})^2 + d_{\pm}, \quad (97)$$

in which R_{\pm} , k_{\pm} and d_{\pm} were identified with the potential energy curve minima, harmonic force constants of the lowest adiabatic double minimum potentials in the avoided crossings quoted above. The coupling function ξ was assumed constant and fitted to the energy gap between the ab initio adiabatic curves at the crossing point. The parameters obtained are listed in table 4. This procedure gives a good potential

Table 4

Model parameters for the curve crossings
in H_2 and in N_2 referred to in the text

	H_2	N_2
m	918.0764	12861.9226
k_-	0.1009	0.1539
k_+	0.0301	1.2534
R_-	1.9287	2.7211
R_+	4.4305	2.1163
d_-	-0.7159	0.4703
d_+	-0.7137	0.4715
ξ	0.0140	5.8E - 03

energy topology for energies below $U_2(R_c)$. We therefore restricted our calculations to vibrational levels below this energy. This gives us a set of fifteen states for H_2 and ten for N_2 . Out of these ten, respectively six, are situated in the crossing region, i.e. in between $U_1(R_c)$ and $U_2(R_c)$.

The exact energy eigenvalues were computed by diagonalizing the coupled diabatic equations in a sufficiently large basis of oscillator states centered at R_c . The corresponding adiabatic energies were obtained by applying the renormalized Numerov method [31] to the adiabatic potential $U_1 + \Delta U_1$. The difference between these numbers gives us the non-adiabatic effect on the vibrational energies. From tables 5 and 6,

Table 5

Overview of computed data for the first fifteen levels in the H_2 case. Exact and adiabatic energies, non-adiabatic effect, GCA energies and percent correction by the GCA of the non-adiabatic effect, and the optimum width parameter of the GCA result. All expressed in a.u.

v	E^{EXACT}	E^{A}	E^{NA}	E^{GCA}	%	W
0	-0.71277456	-0.71276978	-0.4772 E - 05	-0.71277426	93.9	0.129
1	-0.71150141	-0.71150134	-0.7329 E - 07	-0.71150139	74.3	0.077
2	-0.70586208	-0.70586155	-0.5255 E - 06	-0.70586190	65.5	0.088
3	-0.70260842	-0.70257969	-0.2873 E - 04	-0.70260677	94.3	0.139
4	-0.70025733	-0.70025419	-0.3142 E - 05	-0.70025630	67.2	0.109
5	-0.69474660	-0.69473747	-0.9125 E - 05	-0.69474358	66.9	0.121
6	-0.69275543	-0.69265892	-0.9650 E - 04	-0.69275183	96.3	0.144
7	-0.68927111	-0.68920359	-0.6752 E - 04	-0.68926120	85.3	0.151
8	-0.68477073	-0.68460281	-0.1679 E - 03	-0.68475811	92.5	0.151
9	-0.68225661	-0.68200481	-0.2518 E - 03	-0.68224522	95.5	0.158
10	-0.67803302	-0.67771276	-0.3202 E - 03	-0.67799571	88.4	0.167
11	-0.67378367	-0.67339500	-0.3886 E - 03	-0.67376371	94.9	0.158
12	-0.66992495	-0.66944774	-0.4772 E - 03	-0.66987217	88.9	0.167
13	-0.66546969	-0.66487496	-0.5947 E - 03	-0.66536023	81.6	0.167
14	-0.66090423	-0.66032039	-0.5838 E - 03	-0.66085212	91.1	0.158

Table 6

Overview of computed data for the first fifteen levels in the N_2 case. Exact and adiabatic energies, non-adiabatic effect, GCA energies and percent correction by the GCA of the non-adiabatic effect, and the optimum width parameter of the GCA result. All expressed in a.u.

v	E^{EXACT}	E^{A}	E^{NA}	E^{GCA}	%	W
0	0.47186543	0.47186572	-0.291 E - 06	0.47186553	63.6	0.0378
1	0.47501034	0.47509025	-0.799 E - 04	0.47501076	99.5	0.0559
2	0.47529364	0.47531924	-0.255 E - 04	0.47529482	95.4	0.0559
3	0.47865284	0.47868608	-0.332 E - 04	0.47865728	86.6	0.0598
4	0.48184315	0.48196583	-0.122 E - 03	0.48186136	85.2	0.0598
5	0.48395740	0.48428139	-0.323 E - 03	0.48396434	97.9	0.0559
6	0.48606482	0.48643916	-0.374 E - 03	0.48609231	92.7	0.0674
7	0.48921150	0.48976274	-0.551 E - 03	0.48932004	80.3	0.0674
8	0.49246036	0.49312856	-0.668 E - 03	0.49259574	79.7	0.0620
9	0.49544266	0.49617384	-0.731 E - 03	0.49548035	94.8	0.0674

we see that for both molecules the non-adiabatic effect increases by over two orders of magnitude from the ground state to the level nearest $U_2(R_c)$. For all levels in these tables, the GCA energies are computed as a function of W by diagonalizing the GCA integral equation in the set of adiabatic functions obtained from the Numerov method. The typical behaviour of $E^{\text{GCA}}(W)$ is illustrated in fig. 4. Starting from the adiabatic

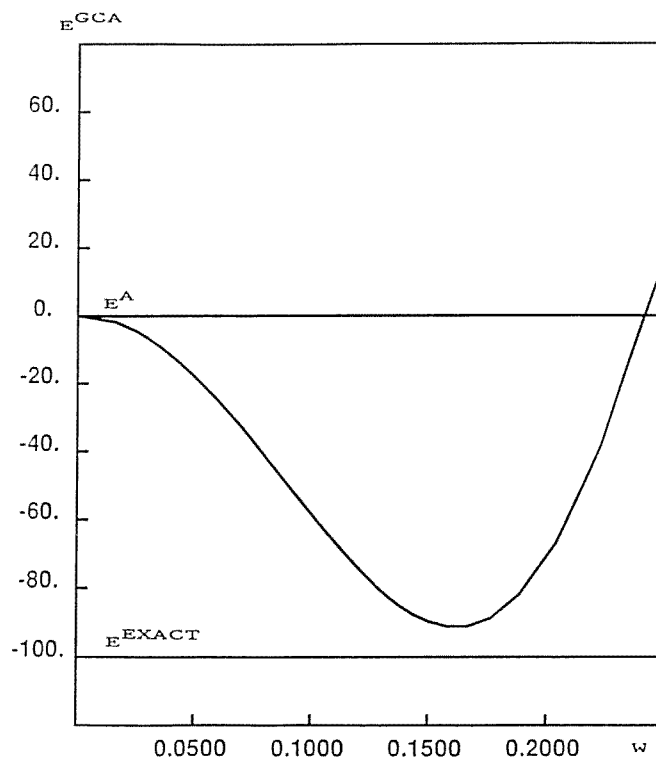


Fig. 4. The GCA energy as a function of W for level $v = 14$ in the H_2 case. The GCA energy is expressed in percent of non-adiabatic effect, W is in a.u.

value at $W = 0$, they show an energy lowering toward the exact values. After reaching a minimum, the curves start to rise due to the more diffuse character of the convolution function. Tables 5 and 6 further list the GCA energies and the values of the width parameters at which they are obtained and give a percentage comparison of the performance of the GCA versus the adiabatic approximation, i.e. the difference between adiabatic and GCA energies relative to the non-adiabatic effect. Overall, there is a marked improvement over the adiabatic results.

If we define the non-GCA effect as the difference between the exact energies and the minima of the $E^{GCA}(W)$, we can compare these numbers with the non-adiabatic effects, as in tables 5 and 6. Because the relative improvement introduced by the GCA is approximately constant as the vibrational quantum number and the non-adiabatic effect increase, the results are even more impressive in absolute terms. This is clearly seen in figs. 5 and 6. They show that the GCA represents an order of magnitude improvement over the adiabatic approximation as far as the levels in the crossing region are concerned.

In order to numerically verify the theoretical statement that in the limit of strong adiabatic coupling the GCA results converge to the exact solutions, we performed

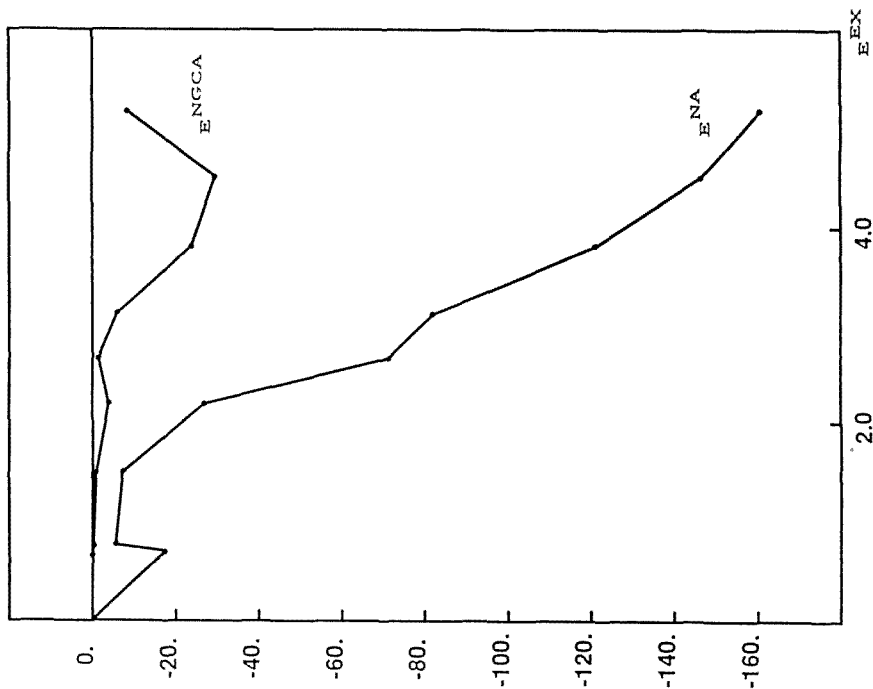


Fig. 5. The non-adiabatic effect E^{NA} and non-GCA effect E^{NGCA} in cm^{-1} versus excitation energy E^{EX} in 10^3 cm^{-1} on the first fifteen levels in the H_2 case.

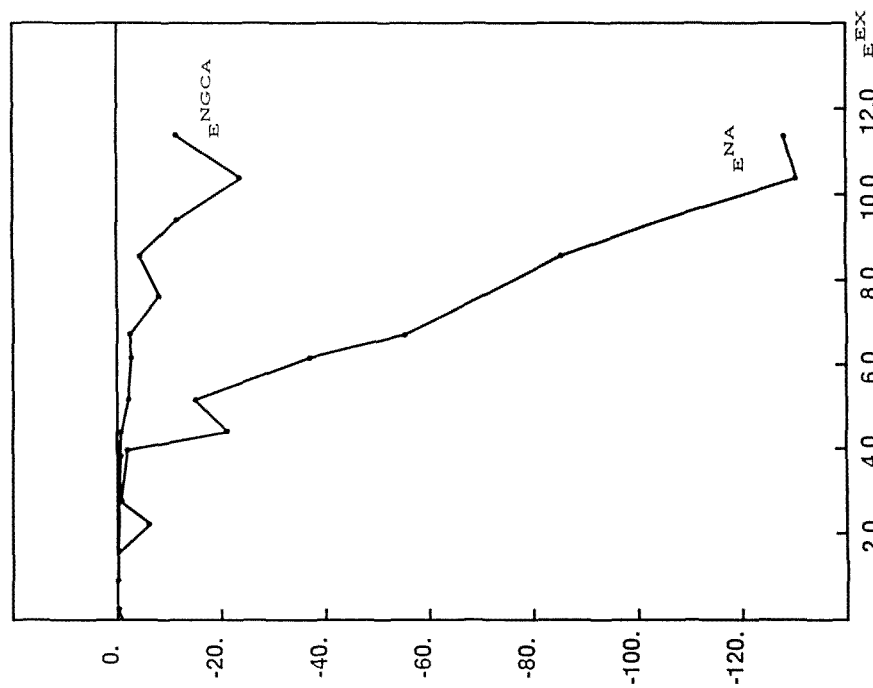


Fig. 6. The non-adiabatic effect (E^{NA}) and non-GCA effect (E^{NGCA}) in cm^{-1} versus excitation energy E^{EX} in 10^3 cm^{-1} on the first nine levels in the N_2 case.

a calculation for H_2 with an energy gap parameter ten times smaller than the one used in the above fit. In table 7, we have listed the non-adiabatic effect in both cases, together with the percentage of the error corrected by the GCA procedure. For the ground state, the non-adiabatic effect in the narrow gap case is extremely small (of order 10^{-8}) and this is the only level in which the GCA percentage did not improve.

Table 7

Comparison of non-adiabatic effects and percentages of non-adiabatic effects corrected by the GCA in the H_2 case for ξ as before, and ξ ten times smaller

ξ	0.014		0.0014	
	E^{NA}	%	E^{NA}	%
v				
0	- 0.4772 E - 05	93.9	- 0.1057 E - 07	79.5
1	- 0.7329 E - 07	74.3	- 0.4067 E - 05	99.0
2	- 0.5255 E - 06	65.6	- 0.2562 E - 06	90.5
3	- 0.2873 E - 04	94.3	- 0.5486 E - 04	99.6
4	- 0.3142 E - 05	67.2	- 0.2990 E - 05	96.3
5	- 0.9125 E - 05	66.9	- 0.1998 E - 04	98.4
6	- 0.9650 E - 04	96.3	- 0.3141 E - 03	99.8
7	- 0.6752 E - 04	85.3	- 0.9548 E - 04	99.1
8	- 0.1679 E - 03	92.5	- 0.2952 E - 03	99.3
9	- 0.2518 E - 03	95.5	- 0.1053 E - 02	99.1
10	- 0.3202 E - 03	88.4	- 0.7495 E - 03	99.0
11	- 0.3886 E - 03	94.9	- 0.1410 E - 02	99.0
12	- 0.4772 E - 03	88.9	- 0.2468 E - 02	98.7
13	- 0.5947 E - 03	81.6	- 0.2433 E - 02	97.9
14	- 0.5838 E - 03	91.1	- 0.3427 E - 02	96.1

However, as one moves into the crossing region the non-adiabatic effect increases by over five orders of magnitude (of order 10^{-3}) and we see that for most levels, especially the ones in the crossing region, the percentages are as high as 95–99. We can safely conclude that the results of table 7 confirm our theoretical findings. The large GCA percentage for levels near the crossing point demonstrate the specific effectiveness of the trial state in crossing situations.

Finally, table 8 lists the exact and adiabatic energies in the strong adiabatic coupling limit $\xi = 0$. As discussed above, the finite non-adiabatic effect is caused by the discontinuity at R_c of the adiabatic correction term. Observe that the magnitude of the non-adiabatic effect increases monotonically with decreasing ξ . The non-adiabatic effect causes drastic level shifts. Indeed, on the 7th level in the left well it is almost as large as the vibrational level spacing. The situation only becomes worse for higher excitations until there is no resemblance left between the adiabatic and exact spectra, and the "breakdown" of the adiabatic approximation is complete.

Table 8

Exact and adiabatic energies and the non-adiabatic effect in H_2 in the strong adiabatic coupling limit, i.e. ξ going to zero

Left well			Right well		
E^{EXACT}	E^A	E^{NA}	E^{EXACT}	E^A	E^{NA}
-0.7106583	-0.7106519	-0.64 E - 05	-0.7108371	-0.7108370	-0.10 E - 06
-0.7001747	-0.7000927	-0.82 E - 04	-0.7051111	-0.7051107	-0.35 E - 06
-0.6896912	-0.6892429	-0.45 E - 03	-0.6993852	-0.6993809	-0.43 E - 05
-0.6792077	-0.6777842	-0.15 E - 02	-0.6936594	-0.6936305	-0.29 E - 04
-0.6687242	-0.6655510	-0.32 E - 02	-0.6879334	-0.6878074	-0.13 E - 03
-0.6582408	-0.6525809	-0.57 E - 02	-0.6822075	-0.6818197	-0.39 E - 03
-0.6477573	-0.6389889	-0.88 E - 02	-0.6764817	-0.6755794	-0.91 E - 03

6.4. SUMMARY

In this section, we have used a model Hamiltonian to simulate curve crossing situations in H_2 and N_2 . We introduced the weak and strong adiabatic coupling limits and showed theoretically that both the adiabatic approximation and the GCA are exact in the weak coupling limit. However, the adiabatic approximation breaks down in the strong coupling limit, whereas the GCA is exact also in this case. Numerically, we find that the GCA for both molecules investigated removes a significant part, i.e. 80 to 90 percent, of the non-adiabatic effect on levels in the crossing region. For H_2 we demonstrated the behaviour of the approximation schemes in the strong coupling limit.

7. Conclusion

In this paper, we have discussed the GCA as a general approximation scheme for molecules. Just as in the Born–Oppenheimer approximation, this new method is based on the concept of "electronic state". In the traditional approaches, the Hilbert space which accommodates the total molecular wave function is generated through a basis set expansion in electronic states taken at the same nuclear configuration. The new mathematical idea behind the GCA is to generate the trial space of molecular states by superposition of the same electronic states taken at different nuclear configurations. Both spaces have a large amount of overlap, but differ in the way in which the correlation between electronic and nuclear motion is incorporated.

We have shown by specific examples that the new method is both applicable and relevant in the energy region near electronic potential minima as well as in the region of avoided crossings of electronic potentials. As an example of the former situation, we have considered the low energy vibration–rotation spectrum of H_2^+ and as an example of the latter, we have looked at the vibrational levels in double minima potentials of H_2 and N_2 . Both studies, however, differ not only in the topology of

the electronic potential surfaces. In the H_2^+ case, we made a complete ab initio calculation, whereas in the avoided crossing case we used a model Hamiltonian which generates an exactly solvable electronic problem.

It might appear paradoxical that in the ab initio case of H_2^+ the GCA should correct only about 40% of the adiabatic error, while in the H_2 and N_2 cases we could obtain an accuracy of over 80%. The reason is that the GCA relies for its electronic–nuclear correlation effects on just one electronic eigenfunction. Therefore, the results are very sensitive to the quality of this function. In the former case we used a moderately accurate electronic state, whereas in the latter we used the exact ones associated with the model, hence the difference in performance.

Therefore, as far as the future perspectives of the GCA are concerned, it is necessary to distinguish between two levels of application of this theory: either one uses the GCA in the full molecular description, including both electronic and nuclear degrees of freedom, or one introduces the GCA at the stage where the electronic variables have been suppressed by the definition of an effective nuclear Hamiltonian. In realistic applications to larger systems, the former approach seems to become prohibitively numerically intensive. Although the GCA saves the calculation of more than one electronic state, it requires very laborious manipulations of the single electronic wave function, that needs to be quite accurate. The latter approach, using model Hamiltonians, seems to be very promising. Extension of the present applications to multi-level crossings and the introduction of several nuclear degrees of freedom to include Jahn–Teller type effects seem feasible.

In any case, the above outline makes it clear that the GCA is able, through its convolution type trial state, to extract information about several electronic states from a single electronic wave function. Therefore, its fundamental merit resides in the physical mechanism embodied in its mathematical formulation.

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