The adiabatic approximation I. The physical background of the Born-Handy ansatz

WERNER KUTZELNIGG

To cite this article: WERNER KUTZELNIGG (1997) The adiabatic approximation I. The physical background of the Born-Handy ansatz, Molecular Physics, 90:6, 909-916

To link to this article: https://doi.org/10.1080/002689797171904

Published online: 03 Dec 2010.

Submit your article to this journal

Article views: 313

View related articles

Citing articles: 110 View citing articles
The adiabatic approximation

I. The physical background of the Born–Handy ansatz†

By WERNER KUTZELNIGG

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

(Received 10 September 1996; accepted 23 October 1996)

There are two current ways to evaluate the adiabatic corrections to a potential energy hypersurface: firstly a rigorous way in which one starts with the separation of the centre-of-mass motion and where one gets rather complicated expressions in terms of relative coordinates in a molecule-fixed frame, and secondly a pragmatic way, recently advocated by Handy et al., where one starts from a one-term Born ansatz in the laboratory system and arrives at a rather simple expression in terms of nuclear coordinates. In this note it is shown that the latter simple expression can also be obtained rigorously, that is by separating the centre-of-mass motion first. Why the pragmatic approach leads to a correct result, and why the specification of a molecule-fixed frame is not necessary for the evaluation of the adiabatic corrections, are analysed.

1. Introduction

Recently Handy and Lee [1] pointed out that the accuracy of quantum chemical calculations achievable at present for small molecules is such that effects going beyond the Born–Oppenheimer (BO) approximation need to be considered explicitly. They referred to a simple recipe suggested previously [2] for the evaluation of the adiabatic or diagonal corrections and also gave convincing numerical evidence that, in the calculation of the nuclear dynamics on an adiabatic surface, the atomic masses should be used rather than the nuclear masses although the latter appear as natural in the adiabatic framework.

The same working formula as derived and used by Handy et al. for the adiabatic correction has been applied even earlier by Sellers and Pulay [3] and Sellers [4]. These workers quoted the textbook of Davydov [5] for the derivation. There [5] one finds (without reference) a recapitulation of the arguments of Born [6] and Born and Huang [7] on which also the derivation of Handy and co-workers [1, 2] is based. However, [3] contains a strange footnote according to which “there exists another term to account for the change in the center of gravity of the molecule brought about by the electron motion”.

In this paper the physical basis of the pragmatic recipe [1–3] will be presented, while a forthcoming part II will deal with the reasons for the superiority of atomic over nuclear masses.

† Dedicated to the memory of W. Kołos.
Born approach the total wavefunction depending on the nuclear coordinates \( r_n \) and the electronic coordinates \( r_e \) is expanded as

\[
\psi(r_e, r_n) = \sum \psi_k(r_e, r_n) \chi_k(r_n), \tag{1}
\]

where the \( \psi_k \) are a (preferably complete) set of known functions of \( r_e \) that depend parametrically on \( r_n \) and where the \( \chi_k \) are regarded as unknown. The \( \psi_k \) are conventionally chosen as a set of eigenfunctions of the clamped nuclei Hamiltonian, but this is not necessarily a good choice, since this set is usually not complete (without the corresponding continuum functions, which one cannot include anyway).

Both the BO approximation and the adiabatic approximation can be based on choosing a single term in equation (1) (to which one often refers to as a BO ansatz); otherwise the treatment is called non-adiabatic. In the adiabatic approximation no additional assumptions, other than the limitation to a single term in equation (1) are made; this ansatz is taken as a variational trial function. In the BO approximation, terms beyond the leading order in \( m/M \) are neglected. Note that the adiabatic approximation is non-perturbative and must not be understood as a theory rigorously correct to \( O(m/M) \) in the sense of perturbation theory in terms of \( (m/M)^{1/4} \) [9] or \( (m/M)^{1/2} \) [11]. Also the present use of adiabatic approximation as opposed to the BO approximation is different from that in [9].

There is one problem with the expansion (1). Such an expansion would be perfectly valid, if \( \psi(r_e, r_n) \) were a bound-state wavefunction. Then, assuming the \( \psi_k \) complete and orthonormal for any set of values of the parameters \( r_n \), one would have \( (N_e \) is the number of electrons)

\[
\chi_k(r_n) = \int \psi(r_e, r_n) \psi_k(r_e, r_n) d^3 r_e_1 \ldots d^3 r_e_{N_e}. \tag{2}
\]

However, this no longer holds for continuum wavefunctions, and the \( \psi(r_e, r_n) \) for a molecule that we are interested in is necessarily a continuum function since it includes the centre-of-mass (COM) motion. Since it is not sure whether an expansion (1) is a formal solution of the full Schrödinger equation

\[
H(r_e, r_n) \psi(r_e, r_n) = E \psi(r_e, r_n), \tag{3}
\]

it may not be justified [12] to insert equation (1) for \( \psi \) in equation (3), and to project from the left by one member \( \psi_k \) of the set as has been suggested by Born [6] and Born and Huang [7]

\[
\sum \int \psi_k^* H \psi_k d^3 r_e_1 \ldots d^3 r_e_{N_e} \chi_k(r_n) = E \chi_k(r_n) \tag{4}
\]

may not be physically meaningful. Moreover a truncated ansatz of type (1), especially the BO ansatz limited to a single term in equation (1), may not be regarded as an approximation to the exact \( \psi \) in the sense of the variation principle, since the variation principle does not apply to continuum states.

A traditional safe way to avoid this dilemma consists of first separating off the COM motion. The remaining Hamiltonian for the relative motion of nuclei and electrons has then bound-state solutions and the formalism based on equations (2)–(4) can be used. However, everything looks then much more complicated than without separation of the COM, in part because this separation mixes electronic with nuclear coordinates and in part owing to problems with the definition of a molecule-fixed coordinate system. The reviews of Sutcliffe [13] or the standard paper on triatomic molecules [14] give a flavour of the complexity that arises.

On the other hand, the original formalism of Born appears to work in a pragmatic sense [1–4] In doing things that, strictly speaking, one should not do, one arrives at the correct adiabatic corrections, and so in a much simpler way than if one had first separated off the COM motion. This has especially been shown by Handy and co-workers [1, 2] who have based their approach on the work of Born [6] and Born and Huang [7] as well as that of Longuet-Higgins [15] For a similar access see Bratoz [16]. Handy and Lee [1] have also studied the case of the hydrogen atom, where one arrives at the correct adiabatic correction in a somewhat unexpected way. They choose an ansatz for the total wavefunction of the H atom as (now \( r_e \) and \( r_n \) mean the coordinates of a single electron and nucleus respectively)

\[
\psi(r_e, r_n) = \psi(r_e, r_n) \chi(r_n), \tag{5}
\]

where \( \psi(r_e, r_n) \) is the clamped-nucleus wavefunction of a particular electronic state. For the H atom one knows the exact solution, which is of the form

\[
\psi(r, R) = \tilde{\psi}(r) \chi(R), \tag{6}
\]

where \( r \) is the relative and \( R \) the COM coordinate. The main difference between equations (5) and (6) is that equation (6) contains a plane wave factor \( \chi(R) \) describing the free motion of the COM while the corresponding plane wave factor in equation (5) is that corresponding to the free motion of a nucleus. Further, the motion of the electron is associated with a reduced mass in equation (6) but with the original electronic mass in equation (5). In the energy corresponding to equation (6), formally no adiabatic correction appears, but the electronic energy depends on the reduced mass. Nevertheless the electronic energy is obtained from equation (5) with an error \( O(m/M) \), as is intended in the adiabatic approximation. The exact electronic
ground-state energy of H-like ions is (in Hartree units) 
\(- \mu Z^2/2\) with \(\mu = (1 + m/M)^{-1}\). A Taylor expansion in 
m/M to O(m/M) yields the BO energy 
\(- Z^2/2\) and the adiabatic correction \(mZ^2/2M\).

We shall show that the procedure explicitly used by Handy et al. and others is not necessary to arrive at the surprisingly simple result for the adiabatic correction; in fact this result can be derived easily from the rigorous formalism, in which first the COM motion is factored off. The key to this consists of not specifying relative coordinates after the separation of the COM motion, since in terms of these coordinates everything becomes rather complicated. It is also not necessary to worry about the definition of a molecule-fixed coordinate system (which introduces even more complications) if one wants to evaluate adiabatic corrections to the potential energy surface. This need arises only when one wants to treat the nuclear motion explicitly.

In the forthcoming part II of this study [17] we shall show that the adiabatic approximation is, in some sense, inconsistent. It takes care of corrections of \(O(m/M)\) to the electronic energy but ignores analogous corrections to the energy of the nuclear motion (which by itself is already of \(O(m/M)\)) except to that of the COM motion. Corrections beyond the BO approximation to the rovibronic energy levels are hence treated in an unbalanced way if one uses the adiabatic approximation. This is somewhat unexpected and in conflict with the generally accepted picture that the physical content of the adiabatic approximation is that the (fast) electrons follow the (slow) nuclei adiabatically. The formulation of a consistent theory of corrections of \(O(m/M)\) to the vibronic energy levels is very complicated, but the replacement of nuclear masses by atomic masses appears as some approximate simulation of a consistent theory [17].

The adiabatic approximation has some features of a first-order perturbation theory. If one wants to go beyond it, especially for degenerate ground states, the method of effective Hamiltonians for the nuclear motion is appropriate [18–20].

2. The traditional rigorous approach toward the adiabatic correction

We shall in this paper consider electronically non-degenerate states. Only for these is the adiabatic approximation meaningful. Nevertheless we shall need the limitation to non-degenerate states only to justify the assumption that the electronic wavefunction is real. Adiabatic corrections are defined even if, owing to degeneracy or near-degeneracy, the adiabatic approximation becomes poor. We start with the Hamiltonian

\[ H = T_n + T_e + V, \]

\[ T_n = - \sum_{\mu=1}^{N_n} \frac{1}{2 M_{\mu}} \nabla_{\mu}^2, \]

\[ T_e = - \frac{1}{2} \sum_{k=1}^{N_e} \nabla_{k}^2, \]

where \(V\) is a function of the relative coordinates of electrons and nuclei, \(\mu\) counts nuclei, \(k\) counts electrons, \(N_n\) is the number of nuclei and \(N_e\) is the number of electrons. Atomic (Hartree) units are used and the nuclear masses are measured in units of the electron mass \(m\).

The first step in any rigorous treatment is the separation of the COM motion. We define the COM coordinate

\[ R = \left( \sum_{\mu=1}^{N_n} M_{\mu} r_{\mu} + \sum_{k=1}^{N_e} r_{ek} \right) / M \]

as well as the corresponding total mass \(M\) and COM kinetic energy operator \(T_R:\)

\[ M = \sum_{\mu=1}^{N_n} M_{\mu} + N_e, \]

\[ T_R = - \frac{1}{2M} \nabla_R^2. \]

The total wavefunction separates exactly as

\[ \psi_{tot}(\ldots r_{ek} \ldots , \ldots r_{nu} \ldots ) = \psi_{rel}(\ldots q_{ek} \ldots , \ldots q_{nu} \ldots ) \times \chi_{COM}(R) \]

where the \(q_{nu}\) and the \(q_{ek}\) are relative nuclear and electronic coordinates respectively. There are many possible ways to define these. One possibility is to favour one of the original \(r_{nu}\), say \(r_{1n}\), and to measure all other coordinates relative to \(r_{1n}\), that is

\[ q_{nu} = r_{nu} - r_{1n}, q_{ek} = r_{ek} - r_{1n}. \]

The only restriction that we shall observe is that there is a common origin for all \(q_{ek}\), while the \(q_{nu}\) (as well as the common origin of the \(q_{ek}\)) are linear combinations of the \(r_{nu}\) only. The relative Hamiltonian \(H_{rel}\) is then

\[ H_{rel} = H - T_R \]

\[ = - \frac{1}{2} \sum_{\mu=1}^{N_n} m_{\mu v} \nabla_{\mu} \cdot \nabla_{v} - \frac{1}{2} \sum_{j=1}^{N_e} m_{jk} \nabla_{j} \cdot \nabla_{k} - \sum_{\mu=1}^{N_n} m_{\mu k} \nabla_{\mu} \cdot \nabla_{k} + V \]

\[ = T_{rel} + V, \]

with \(\mu, v\) ranging from 1 to \(N_n - 1\), and \(j, k\) from 1 to \(N_e\). The \(m_{\mu v}, m_{jk}, m_{\mu k}\) are constants for a given choice of the internal coordinates. The diagonal elements \(m_{\mu \mu}\) or \(m_{kk}\) are inverse reduced masses. One may choose the internal coordinates such that some or even all off-diagonal
elements disappear, but this is not really relevant for what follows.

We limit our attention to such $H_{rel}$ which have bound-state solutions and we choose $\psi_{rel}$ (normalized to unity) as a trial function to approximate a bound state of $H_{rel}$. It is then justified to consider the expectation value

$$\varepsilon_{rel} = \langle \psi_{rel} | H_{rel} | \psi_{rel} \rangle \chi$$

(15)

while the corresponding (formal) expectation value of $H$ with respect to $\psi_{tot}$ becomes problematic and should rather not be used.

The total energy $\varepsilon_{tot}$ is $\varepsilon_{rel}$ plus the COM energy $p^2/2M$ with $p$ the momentum of the COM motion.

We choose now the BO ansatz (after separation of COM motion)

$$\psi_{rel} = \psi(...e_{ek},...e_{en},...)\chi(...e_{en},...)$$

(16)

(with both $\psi$ and $\chi$ normalized to unity) which, at variance with equation (12), implies a loss of generality, that is defines an approximation. There is still some freedom in the choice of $\psi$. The formally simplest choice is to take $\psi$ as solution of the clamped-nuclei (CN) Schrödinger equation

$$(T_e + V)\psi = E(...e_{en},...)\psi$$

(17)

It does not matter in which coordinate system one solves equation (17). In any case, $E$ will depend only on the $e_{en}$, and $\psi$ on the $e_{en}$ and $e_{ek}$. If we insert equations (14) and (16) into equation (15) we get

$$\varepsilon_{rel} = \langle \chi | -\frac{1}{2} \sum m_{\mu \nu} \nabla_{\mu} \cdot \nabla_{\nu} + E(...e_{en},...) \rangle \chi$$

$$+ \Delta E(...e_{en},...) \langle \chi | \chi \rangle$$

(18)

$$\Delta E(...e_{en},...) = \langle \chi | -\frac{1}{2} \sum (m_{kk} - \delta_{kk}) \nabla_k \cdot \nabla_l$$

$$- \frac{1}{2} \sum m_{\mu \nu} \nabla_\mu \cdot \nabla_\nu$$

$$- \frac{1}{2} \sum m_{\mu \kappa} \nabla_\mu \cdot \nabla_\kappa | \psi \rangle$$

(19)

The integration in equation (19) is over the relative electronic coordinates $e_{ek}$.

The potential, in which the nuclei move, is obviously the CN electronic energy $E$ plus the adiabatic correction $\Delta E$. In deriving equation (19) we have assumed that

$$\langle \psi | \nabla_e \psi \rangle = 0,$$

(20)

which usually holds, at least for non-degenerate and hence real electronic states, since $\nabla_e$ is an anti-Hermitian operator.

The adiabatic correction (19) can be decomposed into four parts:

\begin{align*}
(a) & : \langle \psi | -\frac{1}{2} \sum (m_{kk} - 1) \nabla_k^2 | \psi \rangle \\
(b) & : \langle \psi | -\frac{1}{2} \sum m_{jk} \nabla_j \cdot \nabla_k | \psi \rangle, \quad j \neq k, \\
(c) & : \langle \psi | -\frac{1}{2} \sum m_{\mu \nu} \nabla_\mu \cdot \nabla_\nu | \psi \rangle, \\
(d) & : \langle \psi | -\frac{1}{2} \sum m_{\mu \kappa} \nabla_\mu \cdot \nabla_\kappa | \psi \rangle.
\end{align*}

(21)

Both (a) and (b) result from the COM separation and involve only electronic coordinates; (a) takes care of the change from the electronic to the reduced mass, and (b) is the so-called mass polarization; (c) involves the nuclear coordinates and accounts mainly for the parametric dependence of the electronic wavefunction on the nuclear coordinates. The term (d), which (depending on the molecule and the choice of relative coordinates) is not always present, is mixed electronic–nuclear.

Sometimes the term (a) is most important. For the H atom or H-like ions it is the only one. One can eliminate this term for any system, if one does not choose $\psi$ as solution of the CN Schrödinger equation, but rather from

$$\left( -\frac{1}{2} \sum m_{kk} \nabla_k^2 + V \right) \tilde{\psi} = \tilde{E}(...e_{en},...) \tilde{\psi},$$

(22)

$$m_{kk} = \mu^{-1} = 1 + \frac{1}{M},$$

where $M$ is the mass of the nucleus (in units of the electron mass). In fact, $\tilde{\psi}$ can be obtained from $\psi$ by a simple scaling:

$$\tilde{\psi}(...e_{ek},...e_{en},...) = \mu^{3N_e/2} \psi(...\mu e_{ek},...\mu e_{en},...),$$

$$\tilde{E}(...e_{en},...) = \mu E(...\mu e_{en},...).$$

(23)

This is equivalent to using reduced (mass-dependent) atomic units or taking a mass-dependent Rydberg constant, which is certainly customary in atomic theory. In proceeding in this way, one gets the eigenfunction of H-like ions exactly; however, for other systems one can only eliminate the correction (a) and one must evaluate the other corrections (b)–(d) as expectation values, that is in a perturbation-like way. One may regard this as an unbalance and prefer to treat all corrections at the same level, via equation (21). A generalization of equation (22) to molecules has been discussed by Fröman [21]. This leads beyond the adiabatic approximation, without being non-adiabatic.

Equation (19) has been used by Kolos and Wolniewicz [22] for the evaluation of the adiabatic corrections of the $H_2$ molecule to high accuracy.
3. An alternative rigorous approach

Let us now start as in section 2, that is we first separate off the COM motion. However, we do not worry about a definition of relative coordinates (which is to a large extent arbitrary anyway) and leave these coordinates unspecified. We hence write $H_{rel}$ simply as

$$H_{rel} = H - T = T_n + T_e + V = T_{rel} + V. \quad (24)$$

We make again the BO ansatz (16) and consider the expectation value (15), which now looks like

$$\varepsilon_{rel} = \langle \chi | T_n - T_R + E(\ldots \varphi_{nu} \ldots) + \Delta E(\ldots \varphi_{nu} \ldots) | \chi \rangle, \quad (25)$$

$$\Delta E = \langle \psi | T_{rel} - T_e | \psi \rangle = \langle \psi | T_n - T_R | \psi \rangle. \quad (26)$$

Since $\psi$ does not depend on the COM coordinates, $T_R$ has no effect in equation (20), and we can simply write

$$\Delta E = \langle \psi | T_n | \psi \rangle = -\frac{1}{2} \psi \sum \frac{1}{M_\mu} \nabla_{\mu}^2 | \psi \rangle. \quad (27)$$

In this way we have found an extremely simple but rigorous derivation of the compact result, derived previously [2, 5, 15, 16] in a somewhat less rigorous way, and chosen in practical applications by Sellers and Pulay [3] and Sellers [4] as well as by Handy et al. [2].

The present derivation of equation (27) is so simple that it is hard to believe that it has not been known before. There is no extra term as suggested in the footnote in [3]. In equation (27) the physically plausible classification (21) of the adiabatic corrections into various types is lost. However, one has gained that for the evaluation of the adiabatic corrections it is not necessary to specify a molecule-fixed coordinate system, nor to define a non-redundant set of internal coordinates. This is only needed if one wants to study the nuclear dynamics explicitly.

The key for the derivation of equation (27) is that the electronic wavefunction $\psi$ does not depend on the COM coordinates and that hence

$$\langle \psi | T_R | \psi \rangle = 0. \quad (28)$$

This is a direct consequence of the COM separation in section 2. In fact the $\psi$ in sections 2 and 3 are identical. One even sees directly that both the CN Hamiltonian and the CN wavefunction depend only on differences of coordinates (e.g. $r_{nu} - r_{ek}$ or $r_{ek} - r_{ej}$) and are hence independent of the COM. Equation (27) holds independently of the coordinate system in which $\psi$ and $T_n$ are expressed. One possibility is to express $\psi$ in internal coordinates and $T_n$ in a laboratory-fixed coordinate system.

As simple and straightforward as this section looks, it has not been so easy to arrive at it.

4. The Born–Handy ansatz

Handy and co-workers [1, 2] have never claimed to have invented the ansatz referred to here as the ‘Born–Handy ansatz’, but they certainly convinced a large audience that this ansatz is of enormous practical value, even if it has not been completely obvious why it leads to correct results. Handy and co-workers realized that the difficulties with the traditional approach come from the separation of the COM motion (and the need to define internal coordinates after this separation has been made). They therefore decided to renounce this separation. They chose the ansatz very much as originally proposed by Born [6] and reviewed by Longuet-Higgins [15]

$$\psi_{BH} = \psi(\ldots r_{ek} \ldots, \ldots r_{nu} \ldots) \chi(\ldots r_{nu} \ldots) \quad (29)$$

and considered the expectation value

$$\varepsilon_{BH} = \langle \psi_{BH} | H | \psi_{BH} \rangle \langle \chi \rangle. \quad (30)$$

This is strictly not allowed for a continuum function which $\psi_{BH}$ necessarily is. If we construct this expectation value as if this were allowed (taking the CN electronic wavefunction $\psi$ normalized to unity) we get

$$\varepsilon_{BH} = \langle \chi | T_n + E(\ldots \varphi_{nu} \ldots) + \Delta E | \chi \rangle, \quad (31)$$

$$\Delta E = \langle \psi | T_n | \psi \rangle, \quad (32)$$

noting that $\chi$ is a non-normalizable wavefunction.

Obviously the potential in which the nuclei move is the CN energy plus the adiabatic correction $\Delta E$ (equation (32)), in the same form as derived in the previous section.

If, in a next step, we want to study the nuclear motion in the framework of the Born–Handy ansatz, we must now separate off the COM motion for the purely nuclear problem, that is, we write

$$\tilde{\chi} = \chi_{COM}(R_n) \chi(\ldots \varphi_{nu} \ldots), \quad (33)$$

where $R_n$ is the COM of the nuclei given by

$$R_n = \sum_{n} M_\mu r_{nu} / M_n, \quad M = \sum M_\mu \quad (34)$$

and $M_n$ is the total mass of the nuclei.

Then we get

$$\varepsilon_{BH} = \varepsilon_{rel} + \frac{\rho^2}{2M_n}, \quad (35)$$

where $\varepsilon_{rel}$ is given by equation (18) or (25). The only extra error that we make (with respect to the rigorous adiabatic treatment of section 2 or 3) is that the total COM motion is replaced by the motion of the COM of
the nuclei only. This error is of \(O\left(\frac{m}{M}\right)^2\) with respect to the electronic energy and hence negligible in the spirit of the adiabatic approximation.

Handy and co-workers [1, 2] have used the general expression (32) as starting point to derive working formulae in terms of the know-how of gradient techniques. For other approaches on similar lines, see [3, 4, 23].

5. Relation of the Born–Handy ansatz to a rigorous treatment

One can raise two objections against the Born–Handy approach, namely firstly that one tries to manipulate a continuum function as if it were that of a bound state, and secondly that one does not describe the COM motion correctly. One can remove the first objection in the following way. We make the factorization (33) at the beginning rather than at the end. We hence rewrite (29) as

\[ \psi_{BH} = \chi_{COM}(\mathbf{R}_n) \psi_{rel}, \]

\[ \psi_{rel} = \chi(\ldots \mathbf{q}_{nu} \ldots) \psi(\ldots \mathbf{q}_{ek} \ldots, \ldots \mathbf{q}_{nu} \ldots). \]

\( \psi_{rel} \) is the same as in sections 2 and 3. We obtain an energy expression analogous to equations (35) and (25):

\[ \varepsilon_{tot} = \frac{\mathbf{p}^2}{2M_n} + \langle \chi | T_n - T_R + E(\ldots \mathbf{q}_{nu} \ldots) \rangle + \Delta E(\ldots \mathbf{q}_{nu} \ldots) \langle \chi | \psi_n \rangle. \]

To arrive at the simple result (39), one has to use the same trick as in section 3, namely to leave the relative coordinates unspecified. In fact the only difference in the present treatment from that of section 3 is that \( \chi_{COM}(\mathbf{R}) \) is replaced by \( \chi_{COM}(\mathbf{R}_n) \), which no longer appears to present any advantage.

There is still another way to look at the Born–Handy ansatz (29). Let us postulate tentatively that any acceptable approach has to start with a correct factorization of the COM motion. We hence start from the following counterpart of equation (12):

\[ \psi_{BH} = \tilde{\psi}_{rel} \chi_{COM}(\mathbf{R}). \]

In order that equation (40) agrees with equations (29) and (33), we must, in view of equation (16) require that

\[ \tilde{\psi}_{rel} = \frac{\psi_{rel} \chi_{COM}(\mathbf{R}_n)}{\chi_{COM}(\mathbf{R})}. \]

We note that \( \chi_{COM} \) is a plane-wave function; hence (taking the same \( \mathbf{p} \) in both functions)

\[ \frac{\chi_{COM}(\mathbf{R}_n)}{\chi_{COM}(\mathbf{R})} = \exp \left[ \mathbf{p} \cdot (\mathbf{R}_n - \mathbf{R}) \right] \]

\[ = \exp \left[ \mathbf{i} \left( \frac{\sum_k M_k \mathbf{r}_{nu} - \mathbf{M}_n \sum_k \mathbf{r}_{ek}}{\mathbf{M}_n (\mathbf{M}_n + N_c)} \right) \right]. \]

Let us, to simplify the following illustration, assume that the electronic coordinates are measured with respect to the COM of the nuclei, that is

\[ \mathbf{q}_{ek} = \mathbf{r}_{ek} - \sum_k M_k \mathbf{r}_{nu}. \]

Then

\[ \frac{\chi_{COM}(\mathbf{R}_n)}{\chi_{COM}(\mathbf{R})} = \exp \left[ - \mathbf{i} \left( \sum_k \mathbf{q}_{ek} \right) \right]. \]

If we now factorize \( \tilde{\psi}_{rel} \) in analogy to equation (16) we get

\[ \tilde{\psi}_{rel} = \tilde{\psi}(\ldots \mathbf{q}_{ek} \ldots, \ldots \mathbf{q}_{nu} \ldots) \chi(\ldots \mathbf{q}_{nu} \ldots), \]

\[ \tilde{\psi} = \psi \exp \left[ - \mathbf{i} \left( \sum_k \mathbf{q}_{ek} \right) \right]. \]

with \( \psi \) the CN wavefunction, that is the correct electronic wavefunction \( \psi \) in equation (16) is replaced by \( \tilde{\psi} \), which depends on the momentum of the COM motion.

The energy corresponding to equation (40) is the correct COM energy \( \mathbf{P}^2/2\mathbf{M} \) plus the expectation value of \( \tilde{\psi}_{rel} \) including the adiabatic corrections.

There is an addition to the electronic energy given by

\[ \sum_i (\langle \tilde{\psi} | T_{ek} | \tilde{\psi} \rangle - \langle \psi | T_{ek} | \psi \rangle) = N_c \frac{\mathbf{p}^2}{2\mathbf{M}}. \]

and one to the adiabatic diagonal correction given by

\[ \sum_i (\langle \tilde{\psi} | T_{nu} | \tilde{\psi} \rangle - \langle \psi | T_{nu} | \psi \rangle) \]

\[ = \sum_i \frac{1}{2M_{\mu}} \left( \nabla_{nu} \exp \left[ \mathbf{i} \left( \sum_k \mathbf{q}_{ek} \right) \right] \right) \times \left( \nabla_{nu} \exp \left[ - \mathbf{i} \left( \sum_k \mathbf{q}_{ek} \right) \right] \right) \]

\[ = \sum_i \frac{1}{2M_{\mu}} \left( \nabla_{nu} \exp \left[ - \mathbf{i} \left( N_c M_{\mu} r_{nu} \right) \right] \right) \times \left( \nabla_{nu} \exp \left[ \mathbf{i} \left( N_c M_{\mu} r_{nu} \right) \right] \right) \]

\[ = \frac{N_c^2 \mathbf{p}^2}{2\mathbf{M}^2 (2\mathbf{M}_n)^2} \sum_i M_{\mu} = \frac{N_c^2 \mathbf{p}^2}{2\mathbf{M}^2 (2\mathbf{M}_n)^2}. \]
The electronic contribution to the COM motion appears here as an oscillatory factor in the electronic wave-function. The second objection raised against the Handy ansatz is the kinetic energy of the movement of the COM of the nuclei alone, but with the same momentum \( p \), just as it appears in the Born–Handy ansatz. This result is also obtained, if we do not make the special choice (43), but then also the wavefunction of the relative nuclear motion \( \chi(\ldots \mathbf{R}_n \ldots) \) becomes \( p \) dependent. Conversely we can express the wavefunction \( \psi_{\text{tot}} \) (12) through the Born-Handy ansatz \( \psi_{\text{BH}} \) and the inverse of the factor (42), that is for the choice (43) as

\[
\psi_{\text{tot}} = \psi_{\text{BH}} \exp \left[ ip \cdot \left( \sum_k \frac{\mathbf{q}_{ek}}{M} \right) \right]
\]

\[
= \chi_{\text{COM}}(\mathbf{R}_n) \chi(\ldots \mathbf{R}_n \ldots) \tilde{\psi}(\ldots \mathbf{q}_{nu} \ldots, \ldots \mathbf{q}_{ek} \ldots)
\]

\[
\tilde{\psi} = \psi \exp \left[ ip \cdot \left( \sum_k \frac{\mathbf{q}_{ek}}{M} \right) \right].
\]

The electronic contribution to the COM motion appears here as an oscillatory factor in the electronic wavefunction.

The second objection raised against the Handy ansatz, namely that it does not describe the COM motion correctly, will appear less serious, after we have found out that generally the adiabatic approximation makes a similar error for the relative motion of the nuclei [17].

### 6. Concluding remarks

The BO approximation, as it is currently understood, is a recipe that tells us to proceed in two steps. In the first step the electronic Schrödinger equation is solved for CN. In the second step one makes the BO ansatz (29) but ignores the dependence of the electronic wavefunction \( \psi \) on the nuclear coordinates. This leads to a Schrödinger equation for the movement of the nuclei with the electronic energy as the potential. Although the BO approximation was conceived for molecules, what it means is best understood if we apply it to the H atom. In the first step we get the electronic energy as \(- Z^2 / 2n^2\) instead of the correct energy \(- Z^2 \mu / 2n^2\) of the relative motion; in the second step the energy \( p^2 / 2m \) of the nuclear motion instead of the energy \( p^2 / 2M \) of the COM motion is obtained. In either step we make a relative error of \( O(m/M) \), but the absolute error in the second step is smaller by \( O(m/M) \) compared with that of the first step.

In the adiabatic approximation, one chooses the same first step and enters the second step with the same ansatz for the wavefunction, but one no longer ignores the dependence of \( \psi \) on the nuclear coordinates. This requires that one regards equation (29) as a variational ansatz, which is problematic since \( \psi \) is a non-normalizable wavefunction. A safe way consists of first separating off the COM motion. This leads to complicated expressions for the adiabatic corrections in the traditional formulation. However, if one does not specify internal coordinates too early, a very simple expression is obtained, the same as one gets following Handy and co-workers, choosing the original Born ansatz without the COM separation.

So this separation has, when done in the appropriate way, no disadvantage. Nevertheless the question arises whether the COM separation (which is exact) is in the spirit of the BO approximation. In fact, the COM separation mixes electronic and nuclear coordinates, which is in conflict with the philosophy of the (approximate) adiabatic separation. Of course, unlike the COM separation, the adiabatic separation is an approximation. This approximation implies that one gets corrections to the electronic energy of \( O(m/M) \), but that one does not get kinematic corrections to the nuclear motion, the latter being described as in the BO approximation, except for the adiabatic correction to the potential. Separating off the COM motion we do get a relative correction of \( O(m/M) \) to the COM motion, but we do not get a similar correction to the energy of the relative motion of the nuclei (rotation and vibration).

The adiabatic approximation with COM separation is good for atoms, because it takes care that the electrons participate in the COM motion. However, it is unbalanced for molecules, because it favours the COM motion with respect to other motions dominated by the nuclei, such as rotation and vibration, where the participation of the electrons is less trivial anyway than in the COM motion. The partial participation of
the electrons in these motions is ignored in the adiabatic approximation both with and without COM separation. This is the starting point for part II of this series, which is related to the question of whether it is better to use nuclear or atomic masses in a study of the nuclear dynamics.

The author thanks N. C. Handy, B. T. Sutcliffe, V. Staemmler, R. Jaquet, W. Cencek and Ch. van Wullen for fruitful discussions on this subject. He is particularly grateful to N. C. Handy for communicating his unpublished lecture notes on the adiabatic approximation.

References