

# The Born-Oppenheimer Approximation Revisited

Hubert Klar

University of Freiburg, Freiburg im Breisgau, Germany

Email: mail contact hubklar@aol.com

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## Abstract

We present an improved Born-Oppenheimer method for the treatment of molecules. Our development is based on taking into account a portion of the kinetic energy which was inadvertently omitted by Born and Oppenheimer. Our theory replaces the set of standard atom-atom potentials by an evolution operator. In particular, in contrast to the traditional Born-Oppenheimer method our amended basis describes the so-called Wannier phenomenon which deforms potential surfaces, and traps one or more threshold electrons into an unstable equilibrium. Within our framework that trapping manifests itself as a Fresnel distribution. Finally we discover a  $\pi/2$  phase jump in the evolution operator caused by the diffraction of a two-electron wave from a potential ridge.

## Keywords

Born-Oppenheimer, Adiabaticity, Wannier Phenomenon

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## 1. Introduction

Since a century molecules are usually treated within the Born-Oppenheimer (hereafter shorty BO) approximation [1], that method has been also used to solve other nonseparable problems like many-electron atoms in terms of hyperspherical coordinates [2] [3]. Usually the community believes that the success of the BO method rests on the existence of a small parameter like the electron to nucleus mass ratio. That is, however, not quite true. Important for the validity of the BO approximation is a smooth variation of the electronic Hamiltonian as function of the internuclear separation. That property rather than a small numerical parameter delivers a weak non-adiabatic channel coupling. In atomic and molecular applications is that mostly the case due to smooth Coulomb interactions.

There are, however, situations where BO breaks really down. This is, for instance, the case at ionization/dissociation thresholds. Threshold ionization of  $H$  by electron impact was investigated long ago by Wannier [4] in terms of classical mechanics. Its quantum analog is entirely foreign to BO. Further, electronic transitions are not described by the BO standard basis. It is therefore the aim of this paper to develop a better basis which removes these shortcomings. At the time when the BO paper was written there was due to the experimental situation no need to treat such critical situations. However, today there are much more sophisticated experimental possibilities available. Therefore, there is a need for an improvement of the BO technique. Before we go into the new development we summarize shortly the standard BO procedure.

To this end we consider a non-rotating diatomic molecule with nuclear masses  $m_A$  and  $m_B$ , charges  $Z_A$  and  $Z_B$ , respectively. Its center-of-mass Hamiltonian reads

$$H = -\frac{1}{2M} \frac{\partial^2}{\partial R^2} + \frac{Z_A Z_B}{R} + h(r; R) \quad (1)$$

where  $M$  is the reduced mass of the two nuclei;  $R$  is the internuclear separation;  $r$  summarizes all electron coordinates; and  $h(r; R)$  is the electronic part of the Hamiltonian. The latter contains the kinetic energy of all electrons, all electron-nuclei interactions, and all electron-electron interactions. We consider here only light nuclei in nonrelativistic description, *i.e.* with pure Coulomb interactions.

The standard BO strategy is as follows. Because of the big mass of the nuclei they may be regarded to be at rest during the electrons motion. Therefore one constructs in a first step electronic eigenfunctions with nuclei at rest, *i.e.*

$$h(r; R)\Phi^{\text{BO}}(r; R) = U(R)\Phi^{\text{BO}}(r; R) \quad (2)$$

where the eigenvalue  $U(R)$  plays the role of an atom-atom potential.

BO use then a product form for the whole wave function,

$$\Psi(r; R) = F(R)\Phi^{\text{BO}}(r; R). \quad (3)$$

Mathematically, the above  $U$  plays the role of a separation parameter. Substitution of (2) into (1) delivers easily the nuclear wave equation given by

$$-\frac{1}{2M} \frac{d^2 F}{dR^2} + \left( \frac{Z_A Z_B}{R} + U(R) - E \right) F(R) = 0. \quad (4)$$

The last step would be correct provided we were allowed to neglect the derivative terms

$$\frac{\partial \Phi}{\partial R} \quad \text{and} \quad \frac{\partial^2 \Phi}{\partial R^2}. \quad (5)$$

BO were aware of that point. However they claim that the terms (5) are small because of the small parameter  $1/M$ . That statement is indeed correct for the lower well separated channels; actually the BO channels are coupled by the derivative terms (5). It is important to realize that the electron's motion occurs in a

moving frame even if that motion is slow. The motion occurs along the nuclear separation coordinate  $R$ . As novelty Section 2 takes the nuclear motion into account.

## 2. New Development

The above sketched BO derivation suffers from one weak point as may be seen below. It was assumed that the kinetic energy of the whole complex is equal to the sum of nuclear kinetic energy and electronic kinetic energy. That conclusion, however, is not true within the frame of a product wavefunction (3). The following trivial calculation shows

$$\frac{1}{2M} \frac{d^2}{dR^2} \{F(R)\Phi(r;R)\} = \frac{1}{2M} \frac{d^2 F}{dR^2} + \frac{1}{2M} \frac{\partial^2 \Phi}{\partial R^2} + \frac{1}{M} \frac{dF}{dR} \frac{\partial \Phi}{\partial R} \quad (6)$$

The standard version of the BO procedure disregards the last two terms in (6). Born and Oppenheimer were aware of these terms which describe non-adiabatic couplings. The authors claim that these terms are small because of the mass ratio.

It is, however, clear from (6) that all three portions carry the same mass ratio factor. Further it is not evident that the channel functions  $\Phi$  depend only weakly on  $R$ . Below we will see that particularly the last term, a momentum-momentum coupling causes electronic transitions. Moreover, that coupling produces the Wannier phenomenon, *i.e.* an unusual phenomenon caused by equilibrium electronic configurations. Therefore it is the aim of this paper to take that momentum-momentum coupling  $\frac{1}{M} \frac{dF}{dR} \frac{\partial \Phi}{\partial R}$  into account, too.

To this end we modify the l.h.s. of the channel Equation (2) into

$$\frac{1}{M} \frac{dF}{dR} \frac{\partial}{\partial R} + h(r;R) \quad (7)$$

Note, however, that the radial function  $F$  is not yet known in (7). Its derivative we can, however, express by its logarithmic derivative corresponding to an  $R$ -matrix, *i.e.* we write

$$\frac{dF}{dR} = \frac{dR}{F} F \quad (8)$$

and employ, following Sommerfeld [5], an *Abstrahlungsbedingung*<sup>1</sup>, *i.e.* we address that condition to a specific collision channel labelled below by the index  $\mu$ , and use above the  $\mu$ -threshold

$$\frac{F'}{F} = ik_\mu \quad (9)$$

where  $k_\mu = \pm\sqrt{2E_\mu}$  is the wavenumber in the collision channel labelled by  $\mu$ .

Along these lines we arrive at

$$F \left\{ \frac{ik_\mu}{M} \frac{\partial}{\partial R} + h(r;R) \right\} \Phi(r;R) \quad (10)$$

<sup>1</sup>Sommerfeld [5] used (9) in the context of emitted radiation. We do it here for particles.

Because the operator in curly brackets (10) depends on all coordinates there exists no longer a  $R$ -dependent potential but (10) must be equal to a constant  $\mathcal{E}$ . As part of the Hamiltonian this constant has the dimension of an energy. For a finite radial function  $F$  we complete expression (10) to the equation

$$\left\{ \frac{ik_{\mu}}{M} \frac{\partial}{\partial R} + h(r; R) \right\} \Phi(r; R | \mathcal{E}) = \mathcal{E} \Phi(r; R | \mathcal{E}) \quad (11)$$

where we employ  $\mathcal{E}$  to be any energy level of the whole  $(N-1)$ -electron system.

The l.h.s. of (11) has the structure of a time-dependent wave equation where time  $t$  has been replaced by the separation  $R$ . Therefore (11) describes an evolution, for instance from the united atom limit to the limit of separated atoms. We rewrite (11) for convenience as

$$\left\{ \frac{ik_{\mu}}{M} \frac{\partial}{\partial R} + h(r; R) - \mathcal{E} \right\} \Phi(r; R | \mathcal{E}) = 0 \quad (12)$$

Thus we intend to solve (12) with the Ansatz

$$\Phi(r; R | \mathcal{E}) = E(R, 0) \Phi(r; 0 | \mathcal{E}) \quad (13)$$

where  $\Phi(r; 0 | \mathcal{E})$  is an eigenstate of the system in the united atom limit with energy  $\mathcal{E}$ . The evolution operator satisfies then the same equation as (11), *i.e.*

$$\left\{ \frac{ik_{\mu}}{M} \frac{\partial}{\partial R} + h(r; R) - \mathcal{E} \right\} E(R, 0) = 0. \quad (14)$$

(14) may be regarded as a generalization of the Born-Oppenheimer equation (2) as may be seen as follows. Actually, if we confine ourselves to standing wave solutions we rediscover the BO eigenvalue problem as may be seen as follows. If the operator  $h(r; R)$  depends only weakly on  $R$  we can solve our equation (11) with help of a phase, *i.e.* we put

$$\Phi(r, R | \mathcal{E}) = \exp \left\{ -\frac{i}{2} \int^R k_{\mu}(R') dR' \right\} \bar{\Phi} \quad (15)$$

Substitution into (11) or (12) delivers immediately after identification of  $\mathcal{E} = E$  the standard BO eigenvalue equation

$$h(r; R) \bar{\Phi} = U(R) \bar{\Phi} \quad (16)$$

So far we have apparently nothing new. But that consideration overlooks that (16) delivers only a discrete spectrum of standing wave solutions representing bound states. (16) fails, for example, to describe ionization by a charged collision partner. The next §3 demonstrates, however, that our evolution operator does more; it delivers indeed a key non-standing wave solution describing threshold ionization, too.

Entirely different is the situation for an ionizing collision with a charged collision partner at low energy, *i.e.* near threshold. We are then confronted with three charged particles in the continuum at nearly zero energy. We know from inelastic electron atom scattering that we are confronted in that situation with

the so-called Wannier [4] phenomenon. This is foreign to the standard BO approximation, but the next section will show that our evolution operator describes that critical situation as well.

### 3. Example: $H(n \geq 1)$ + Bare Nucleus

We illustrate below the power of our method treating as example an ionizing nucleus-atom collision. We use hydrogen as simplest target  $H(nl)$  with principal quantum number  $n \geq 1$  and energy levels

$$E_n = -\frac{1}{2n^2} \quad (17)$$

The  $l$ -degeneracy does not play any role in the following. We focus to high excitation  $n > 1$ , a situation not well treated by the standard BO approximation. At small values of  $n$  the electron performs in the absence of the ion circular Bohr orbits around the proton. At increasing excitation and in the presence of the ion these orbits become deformed. If we increase further the excitation, say  $n \gg 1$  the electron's motion is no longer controlled by the attraction to the proton but it experiences an equilibrium location between the proton and the nucleus which coincides with the nuclear center-of charge. That equilibrium is, of course, unstable. We investigate now what the electron with nearly zero-energy does in such a situation.

To this end we give at first the location of the equilibrium point. The electron-proton separation in that point is

$$r_p = R \frac{Z}{Z+1} \quad (18)$$

whereas the electron-nucleus separation reads

$$r_n = R \frac{1}{Z+1} \quad (19)$$

where  $Z$  is the charge of the colliding nucleus.

Since we intend to explore the threshold region, we determine the evolution operator near the nuclear charge center. The stable Coulomb attraction forces the electron onto the internuclear axis, *i.e.* a collinear model of the whole system is justified. To describe the electron motion in the vicinity of that point we introduce at fixed separation  $R$  a coordinate  $x$  to describe departures from that point. To that end we write for the distances

$$\begin{pmatrix} r_p \\ r_n \end{pmatrix} = \begin{cases} R \frac{Z}{Z+1} (1+x) \\ R \frac{1}{Z+1} (1-x) \end{cases} \quad (20)$$

with  $|x| \leq 1$ . The electronic Hamiltonian reads therefore

$$h(x; R) = -\frac{1}{R^2} \frac{\partial^2}{\partial x^2} + V(x, R) \quad (21)$$

with the total Coulomb potential given by

$$V(x; R) = \frac{1}{R} \left( Z - \frac{Z+1}{1-x} - \frac{Z+1}{Z(1+x)} \right) \quad (22)$$

For small values of  $|x|$ , *i.e.* near the nuclear charge-center this simplifies to

$$V(x; R) \cong -\frac{C_0}{R} - \frac{C_2}{R} x^2 \quad (23)$$

with the net charge on the top of the  $(x, R)$ -potential ridge given by

$$C_0 = \frac{Z^2 - 2Z + 1}{Z} = \frac{(Z-1)^2}{Z} \quad (24)$$

and the curvature across the ridge given by

$$C_2 = \frac{(Z+1)^2}{Z} \quad (25)$$

In (14) we write thus

$$h(x; R) = -\frac{1}{R^2} \frac{\partial^2}{\partial x^2} - \frac{C_2}{R} x^2 \quad (26)$$

and put the ridge charge into the wavenumber now given by

$$k_n = \pm \sqrt{-\frac{1}{2n^2} + \frac{C_0}{R}} \quad (27)$$

At threshold corresponding to  $n \rightarrow \infty$  we put

$$\mathcal{E} = 0 \quad (28)$$

and

$$\lim_{n \rightarrow \infty} k_n = k_\infty = \pm \sqrt{\frac{C_0}{R}}. \quad (29)$$

The equation for the evolution reads therefore

$$\left\{ \pm \frac{i}{M} \sqrt{\frac{C_0}{R}} \frac{\partial}{\partial R} - \frac{1}{R^2} \frac{\partial^2}{\partial x^2} - \frac{C_2}{R} x^2 \right\} E(R, 0) = 0 \quad (30)$$

with the initial condition  $E(0, 0) = 1$ . It is easy to find the solution in the Coulomb zone which extends at threshold to infinity. To this end we put

$$E(R, 0) = \exp\{ic\sqrt{R}x^2\} \quad (31)$$

where  $c$  is a constant to be determined below. Substitution of (31) into (30) confirms our Ansatz (31) with the condition

$$4c^2 \mp \frac{\sqrt{C_0}}{2M} c - C_2 = 0 \quad (32)$$

which may be regarded as a potential surface deformation, in the present case a curvature  $C_2$  deformation.

Equation (32) has two solutions, one for an outgoing wave along  $R$  combined with an outgoing wave across the ridge along  $x$ . That describes an expanding mode near the ridge, and corresponds to Wannier's diverging trajectory. This solution reads

$$c_{diver} = -\frac{\sqrt{C_0 + \frac{C_2}{64M^2}} + \sqrt{C_0}}{16M} \quad (33)$$

The second solution combines incoming waves along  $R$  and  $x$  which represents a dominantly correlated shrinking solution which corresponds to Wannier's converging trajectory whose  $c$ -value is given by

$$c_{conv} = -c_{diver} > 0 \quad (34)$$

The algebraic structure of the evolution (31) resembles a Fresnel distribution [6] denoted in the mathematical literature by...

$$\Delta_\eta = \sqrt{\frac{a}{i\pi\eta}} \exp\left\{\frac{iax^2}{\eta}\right\}. \quad (35)$$

The expression (35) converges to a Dirac delta distribution according to

$$\lim_{\eta \rightarrow 0} \Delta_\eta = \delta(x) \quad (36)$$

valid for  $x \in \mathbb{R}$  and real  $a > 0$ . Therefore, an evolution starting from the united atom attracts the electron to its equilibrium point. Precisely, we get

$$\lim_{R \rightarrow \infty} E(x; R) = \sqrt{\frac{i\pi}{c_{conv}}} R^{-\frac{1}{4}} \delta(x) \Phi(0; R \rightarrow \infty) \quad (37)$$

where we have used  $\eta = 1/\sqrt{R}$  [6]. Moreover, we remark that the threshold evolution (31) delivers on the r.h.s. of (30) the quantity

$$-i \frac{2c}{R^{\frac{3}{2}}} E(R, 0). \quad (38)$$

The Hermiticity of the evolution equation forbids an imaginary eigenvalue like (38). We read, therefore, our (38) in the form

$$-\frac{2c}{R^{3/2}} \exp\left\{i \frac{\pi}{2} + ic\sqrt{R}x^2\right\} \quad (39)$$

That interpretation tells us that the correlated three-body complex has picked up during the converging mode of motion a phase-jump of  $\pi/2$  in consequence of the diffraction from the ridge. An effect similar to ours was reported by Fano [7] when he derived a phase jump due to the embedding of a Feshbach resonance into a continuum. Our quantity  $\frac{-2c}{R^{3/2}}$  may now be regarded as attractive potential curve which crosses all adiabatic BO curves. At these crossings we expect to occur electronic transitions. The evolution reported here plays therefore a catalytic role in electronic excitation processes.

The latter result is entirely foreign to the standard Born-Oppenheimer approximation. In the BO picture this unusual attraction is hidden in the infinity of strongly coupled adiabatic channels. It is remarkable that an electron is attracted to a statically unstable location. The result achieved in §3 represents a novel effect stemming from the diffraction of an electron wave from a many-body potential ridge. Here, we have demonstrated the effect in the simplest case of

three bodies. It is straight forward to generalize the above effect to more electrons and multiply charged ions because; for instance, two or even more than two electrons can be trapped onto multidimensional potential ridges [8]. Finally, we remark that the present development did not use the smallness of any parameter like a mass ratio. Therefore it applies to electron/ion-atom scattering as well where the mass ratio  $1/M$  is close to one.

### Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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