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Does the Born–Oppenheimer Approximation Work?

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Abstract. A model discussion confirms the claim of Born and Oppenheimer on molecular wave functions and spectra.

Almost a half a century ago Born and Oppenheimer [1] devised a method for the computation of molecular wave functions. It turned out to be the key for the interpretation of molecular spectra [2]. As the authors point out, their derivation is mainly supported by its success in reproducing the experimentally known order of magnitude of electronic, vibrational and rotational energies [3]. Mathematically their argument is somewhat mysterious. They not only propose a perturbation theory in a small parameter κ, defined as the fourth root of the electron mass m divided by the mass of the nuclei M, but again make use of the large masses of the nuclei in a semiclassical approximation [4].

More precisely the problem of Born and Oppenheimer is the following: Let H be the Hamiltonian for a system of heavy and light particles:

$$H = \frac{1}{2M}\sum_{i=1}^{N} P_i^2 + \frac{1}{2m}\sum_{l=1} p_l^2 + V(\mathbf{X},\mathbf{x}) \quad \mathbf{X} = (X_1, \ldots, X_N) \quad \mathbf{x} = (x_1, \ldots, x_M), \tag{1}$$

and let H_{cM} be the Hamiltonian of the center of mass motion and $\kappa = \sqrt[4]{m/M}$. How do the eigenvalues W and eigenfunctions ψ of $H' = H - H_{cM}$ depend on κ?

The main hypothesis in their analysis are some analyticity assumptions of the eigenvalues and eigenfunctions as functions of κ^2 and κ respectively. They are not very precisely formulated in their work. In rephrasing their assumptions we use some of the knowledge already gained through the discussion of the model to be described. The analyticity assumptions read as follows: There exists an equilibrium position X° of the heavy particles such that the eigenvalues W and the scaled eigenfunctions $\phi(\xi, x)$ – not the eigenfunctions themselves –

$$\phi(\xi, x) = \kappa^{3/2(N-1)}\psi(\kappa\xi + X^\circ, x) \tag{2}$$

are analytic in κ^2 and κ respectively for fixed m in the neighbourhood of zero. It is this hypothesis, supposedly valid for an arbitrary Hamiltonian of type (1), that will be tested below for a very particular case.

The situation can be rephrased in a more abstract manner: Let $\mathscr{H}$ be the Hilbert space of states $\mathscr{H} = L^2(d^3\mathbf{x}, d^3\mathbf{X})$ and H the Hamiltonian (1). Then there shall exist a unitary group of scale transformations $U(\kappa)$ defined by (2) such that the family of operators $H'(\kappa) = U(\kappa)\, H'\, U^{-1}(\kappa)$ is analytic in κ[1]) at $\kappa = 0$ for m fixed. Notice that the $\kappa \to 0$ limit for H' itself does not necessarily make any sense at all. This will be supported by the model calculation. The unitary group $U(\kappa)$ is constructed to absorb the non-analytic part in H' in the neighbourhood of $\kappa = 0$.

Our model does indeed show the analyticity properties anticipated by Born and Oppenheimer. We wish to point out that the limit $\kappa \to 0$ and m fixed is a singular perturbation even in the otherwise trivial center of mass part of the Hilbert space. The mass of the heavy particles tends to infinity. Therefore we also discuss the situation $\kappa \to 0$ and M fixed, where no such problems appear. This limit might be important for the scattering theory of molecules. The model discussion shows that in this case one has to expect a more singular behaviour of the eigenvalues whereas the eigenfunctions are now better behaved. The results are tabulated at the end of this note.

The model consists of two heavy and one light particle, interacting through harmonic forces:

$$H = \frac{P_1^2}{2M} + \frac{P_2^2}{2M} + \frac{p_1^2}{2m} + A(X_1 - X_2)^2 + a(X_1 - x_1)^2 + a(X_2 - x_1)^2, \tag{3}$$

P_i, X_i, $i = 1, 2$, denote momentum and coordinates of the heavy particles, p_1, x_1 those of the light one. A and a are real numbers parametrizing the strength of the harmonic potentials. We will discuss the spectrum and eigen functions of $H' = H - H_{cM}$, where H_{cM} is the Hamiltonian for the free center of mass motion, as a function of κ for M or m fixed. Introducing Jacobi coordinates[2]), the Hamiltonian splits into two commuting terms:

$$H' = \omega_N(\vec{\mathscr{C}}_N^* \vec{\mathscr{C}}_N + 3/2) + \omega_{\text{el}}(\vec{\mathscr{C}}_{\text{el}}^* \vec{\mathscr{C}}_{\text{el}} + 3/2) \tag{4}$$

$$\omega_N^2 = 2BM^{-1} = 2Bm^{-1}\kappa^4, \quad B = (a + 2A)$$

$$\omega_{\text{el}}^2 = 2aM^{-1}\kappa^{-4}(2 + \kappa^4) = 2am^{-1}(2 + \kappa^4)$$

The $\mathscr{C}$'s are standard Bose operators

$$[\mathscr{C}_N^i, \mathscr{C}_N^{k*}] = \delta_{ik}$$

$$[\mathscr{C}_{\text{el}}^i, \mathscr{C}_{\text{el}}^{k*}] = \delta_{ik}$$

$$[\mathscr{C}_N^i, \mathscr{C}_{\text{el}}^{k\#}] = 0,$$

where # stands for the star or nothing. The spectrum of H' is given by

$$\sigma(H') = \{\omega_N(|\vec{n}| + 3/2) + \omega_{\text{el}}(|\vec{m}| + 3/2)\,|\,\vec{n}\epsilon(Z^+)^3, \vec{m}\epsilon(z^{+3})\}$$

where $|\vec{m}| = \sum_{i=1}^3 m_i$. The eigenfunctions of H' are of the form

$$|\vec{m}, \vec{n}\rangle = \text{polynomial in } (\mathscr{C}_N^i + \mathscr{C}_N^{i*}, \mathscr{C}_{\text{el}}^k + \mathscr{C}_{\text{el}}^{k*})\,\Omega, \quad i = 1, 2, 3. \tag{5}$$

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1) We do not want to specify the type of analyticity for the general Hamiltonian. For the particular model to be discussed we will consider several kinds of analyticity.

2) $\begin{pmatrix} X_1 \\ x_1 \\ X_2 \end{pmatrix} \to \begin{pmatrix} X_{cM} \\ X \\ x \end{pmatrix} = T \begin{pmatrix} X_1 \\ x_1 \\ X_2 \end{pmatrix}, \quad T = \begin{pmatrix} M/\Sigma & m/\Sigma & M/\Sigma \\ 1 & 0 & -1 \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix}$ $\Sigma = 2M + m$, see Figure 1.

Ω denotes the ground state of H'. Of course Ω factorizes into two terms according to (4), $\Omega = \Omega_N \cdot \Omega_{el}$.

$$\Omega_N = \pi^{-3/4} \left(\frac{BM}{2}\right)^{3/8} \exp - \frac{1}{2}\left(\frac{BM}{2}\right)^{1/2} X^2 \tag{6a}$$

$$\Omega_{el} = \pi^{-3/4} (8aM)^{3/8} \kappa^{3/2} (2+\kappa^4)^{-3/8} \exp - \tfrac{1}{2}(8aM)^{1/2} \kappa^2 (2+\kappa^4)^{-1/2} x^2 \tag{6b}$$

$$\Omega = \pi^{-3/2}(4aM^2 B)^{3/8} \kappa^{3/2}(2+\kappa^4)^{-3/8} \exp - \frac{1}{2}\left(\frac{BM}{2}\right)^{1/2} X^2 - \tfrac{1}{2}(8aM)^{1/2}\kappa^2(2+\kappa^4)^{-1/2} x^2. \tag{6c}$$

Substituting $m\kappa^{-4}$ for M one gets

$$\Omega_N = \pi^{-3/4} \left(\frac{Bm}{2}\right)^{3/8} \kappa^{3/2} \exp - \frac{1}{2}\left(\frac{Bm}{2}\right) \kappa^{-2} X^2 \tag{7a}$$

$$\Omega_{el} = \pi^{-3/4}(8am)^{3/8} (2+\kappa^4)^{-3/8} \exp - \tfrac{1}{2}(8am)^{1/2} (2+\kappa^4)^{-1/2} x^2 \tag{7b}$$

$$\Omega = \pi^{-3/2}(4am^2 B)^{3/8}) \kappa^{-3/2}(2+\kappa^4)^{-3/8} \exp - \frac{1}{2}\left(\frac{Bm}{2}\right) \kappa^{-2} X^2 - \tfrac{1}{2}(8am)^{1/2} (2+\kappa^4)^{-1/2} x^2. \tag{7c}$$

Following Born and Oppenheimer we consider not only the eigenfunctions but also the scaled eigenfunctions $\phi(\xi, x) = (U(\kappa)\psi)(\xi, x)$ defined by

$$\phi(\xi, x) = \kappa^{3/2} \psi(\kappa\xi, x). \tag{8}$$

Notice that $U(\kappa)$ is a κ-dependent unitary transformation from the Hilbert space of states $\mathscr{H} = L^2(d^3X, d^3x)$ to the Hilbert space of scaled states $\mathscr{H}_s = L^2(d^3\xi, d^3x)$. In particular one gets easily from (6)

$$(U(\mathrm{x})\,\Omega_N)\,(\xi) = \pi^{-3/4} \left(\frac{BM}{2}\right)^{3/8} \kappa^{3/2} \exp - \frac{1}{2}\left(\frac{BM}{2}\right)^{1/2} \kappa^2 \xi^2$$

$$(U(\mathrm{x})\,\Omega)\,(\xi, x) = \pi^{-3/2} (4aM^2 B)^{3/8} \kappa^3 (2+\kappa^4)^{-3/8} \exp - \frac{1}{2}\left(\frac{BM}{2}\right)^{1/2} \kappa^2 \xi - \tfrac{1}{2}(8aM)^{1/2} \kappa^2 (2+\kappa^4)^{-1/2} x^2. \tag{9}$$

Substituting again $m\kappa^{-4}$ for M one gets

$$(U(\mathrm{x})\,\Omega_N)\,(\xi) = \pi^{-3/4} \left(\frac{Bm}{2}\right)^{3/8} \exp - \frac{1}{2}\left(\frac{Bm}{2}\right) \xi^2$$

$$(U(\mathrm{x})\,\Omega)\,(\xi, x) = \pi^{-3/2} (4am^2 B)^{3/8} (2+\kappa^4)^{-3/8} \exp - \frac{1}{2}\left(\frac{Bm}{2}\right) \xi^2 - \tfrac{1}{2}(8ma)^{1/2} (2+\kappa^4)^{-1/2} x^2. \tag{10}$$

We are now prepared to look at the analyticity of eigenvalues, eigenfunctions and scaled eigenfunctions in κ for m or M fixed. It is readily seen that it is sufficient to look

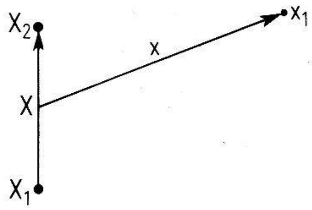

Figure 1
Jacobi coordinates.

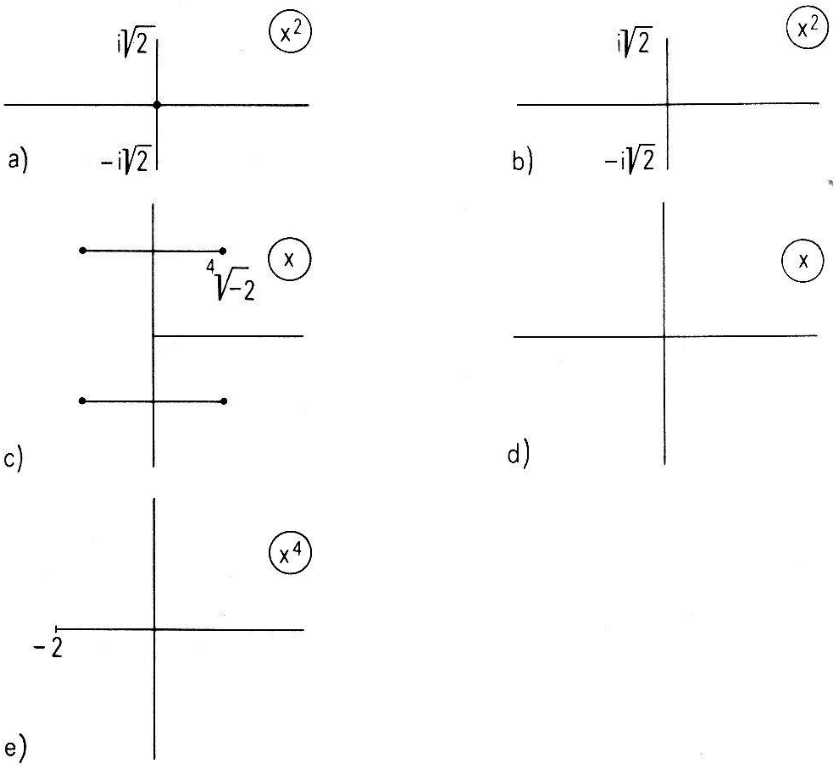

Figure 2
Domains of analyticity for eigenvalues and eigenfunctions, see table.

Table 1
Analyticity of eigenfunctions and eigenvalues

	M fixed	m fixed
Eigenvalues	Analytic in κ^2, first-order pole at $\kappa^2 = 0$, cuts starting at $\kappa^2 = \pm i\sqrt{2}$ (Fig. 2a)	Analytic in κ^2, cuts starting at $\kappa^2 = \pm i\sqrt{2}$ (Fig. 2b)
Eigenfunctions		
a) X, x fixed	Analytic in κ with cuts starting at $\kappa = 0$ and $\kappa = \sqrt[4]{-2}$ (Fig. 2c)	Analytic in κ with essential singularity at $\kappa = 0$ and cuts starting at $\kappa = 0$, $\kappa = \sqrt[4]{-2}$ (Fig. 2c)
b) As elements of $\mathscr{H}$	Analytic in κ for $\operatorname{Re} \kappa^2(2 + \kappa^4)^{-1/2} > 0$, cuts starting at $\kappa = 0$ and $\kappa = \sqrt[4]{-2}$	Analytic in κ for $\operatorname{Re} \kappa^2 > 0$, $\operatorname{Re}(2 + \kappa^4)^{1/2} > 0$, cuts starting at $\kappa = 0$ and $\kappa = \sqrt[4]{-2}$
Scaled eigenfunctions		
a) ξ, x fixed	Analytic in κ with cuts starting from $\kappa = \sqrt[4]{-2}$ (Fig. 2d)	Analytic in κ^4 with cuts starting at $\kappa^4 = -2$ (Fig. 2e)
b) As elements of $\mathscr{H}_s$	Analytic in κ with cuts starting from $\kappa = \sqrt[4]{-2}$ and $\operatorname{Re} \kappa^2 > 0$, $\operatorname{Re}(2 + \kappa^4)^{1/2} > 0$[3])	Analytic in κ^4 with cuts starting at $\kappa^4 = -2$, $\operatorname{Re}(2 + \kappa^4)^{1/2} > 0$[4]) (Fig. 2e)

at the analyticity properties of $\omega_N(\kappa^2)$, $\omega_{el}(\kappa^2)$, $\Omega(\kappa;X,x)$ and $(U(\kappa)\Omega)(\kappa;\xi,x)$. As for the eigenfunctions and the scaled eigenfunctions we consider two aspects of analyticity. The results are tabulated in Table 1. They follow immediately from (5–10). Notice that the analyticity of the scaled eigenfunctions as elements in $\mathscr{H}_s$ can be reformulated as the analyticity of the resolvent of $H'(\kappa) = U(\kappa)\, H'\, U^{-1}(\kappa)$ in the operator norm sense.

Finally, we wish to point out a peculiarity of the model. Each eigenfunction of H' factorizes into an 'electronic term' depending only on x (electronic coordinate) and a 'nuclear term' depending only on X (nuclear coordinate). They are of the so-called adiabatic type. All non-Born–Oppenheimer terms vanish.

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[1] M. Born and R. Oppenheimer, Annalen der Physik *84*, 457 (1927).
[2] S. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company 1962).
[3] Ref. 1, first sentence on page 458.
[4] Ref. 1, equation (16).

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3) The point $\kappa = 0$ is on the boundary of the domain of analyticity.

4) The condition $\mathrm{Re}(2 + \kappa^4)^{1/2} > 0$ determines the Riemann sheet of the function $(2 + \kappa^4)^{1/2}$, i.e. the eigenfunctions are analytic in κ^4 as functions with values in $\mathscr{H}_s$ on one Riemann sheet of $(2 + \kappa^4)^{1/2}$ only.