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Theoretical
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Perspective

Perspective on “Zur Quantentheorie der Molekeln”

Born M, Oppenheimer R (1927) Ann Phys 84: 457

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Abstract. The Born–Oppenheimer approximation, introduced in the 1927 paper “On the quantum theory of molecules”, provides the foundation for virtually all subsequent theoretical and computational studies of chemical binding and reactivity, as well as the justification for the universal “ball and stick” picture of molecules as atomic centers attached at fixed distances by electronic glue.

Key words: Adiabatic – Nonadiabatic – Potential-energy surface – Born-Oppenheimer approximation

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Chemistry is about structure and reactivity. Modern discussions of both these subjects center on the concept of the “potential-energy surface”, $\mathscr{E}(\mathbf{R})$. As illustrated in Fig. 1, $\mathscr{E}(\mathbf{R})$ is the energy of a molecular system or, more generally, of any collection of interacting atoms when the nuclei are fixed at position $\mathbf{R} = \{\mathbf{R}_1, \mathbf{R}_2, ...\}$. For a diatomic molecule, $\mathscr{E}(\mathbf{R})$ is a one-dimensional “potential-energy curve” representing the energy of the molecule as a function of the internuclear distance. The location, R_0, of the minimum energy along the curve is the bond length of the molecule. The energy difference, $\mathscr{E}(\infty) - \mathscr{E}(R_0)$, is the energy required to break the bond, i.e., the bond strength. The curvature at the bottom of the potential well is the force constant that determines the vibrational frequency of the molecule. The bond length, R_0, determines the moment of inertia of the molecule, i.e., its rotational motion. Similarly, for a polyatomic system, stable conformations correspond to local minima of $\mathscr{E}(\mathbf{R})$, for example, points A and B in Fig. 1. The properties of $\mathscr{E}(\mathbf{R})$ in the vicinity of each local minimum govern the vibrational and rotational spectrum and the energetic stability of the conformation. Reactivity is determined by the pathways that lead from one stable minimum to another, or between a minimum and a valley corresponding to separated reactants or products, for example, regions C and D in Fig. 1. The minimum energy path connecting two stable conformers is often identified as the “reaction coordinate”. The saddle point $\mathbf{R}_{ts}$, or position of maximum energy along the minimum energy path, is the “transition state” (point E in Fig. 1.). The properties of $\mathscr{E}(\mathbf{R})$ in the vicinity of $\mathbf{R}_{ts}$ are the input for the widely used “transition-state-theory” or “activated-complex theory” of chemical reaction rates. The actual time-dependent trajectory that the system follows as a reaction progresses (e.g., the solid curve with directional arrows in Fig. 1) is the focus of the field of chemical dynamics. Old chemical bonds may be broken and new ones formed as the system evolves along the trajectory, and dynamical questions can be addressed such as is a long-lived intermediate involved or how is the energy of reaction deposited among the degrees of freedom of the products? (The oscillatory motion of the trajectory in Fig. 1 illustrates vibrational excitation of products).

The above discussion of chemical structure, properties, stability, reactivity and dynamics does not mention the word “electron”. Indeed, when we picture a molecule in our minds, on paper or on the computer screen, we assign positions for each of the nuclei but rarely designate the positions of electrons. The justification for this is the Born-Oppenheimer approximation [1]. In the 1920s the new quantum theory was able to demystify the electronic structure of atoms, even quantitatively for hydrogen; however, molecules exhibit all the electronic complexity of atoms and, in addition, comparably complex interactions among the nuclei. Born and Oppenheimer recognized that a great simplification results because the mass of the electron is much less than that of any nucleon. (The mass of the lightest atom, hydrogen, is 1836 times that of the electron.) To a good approximation (with exceptions, as discussed later) electrons respond instantaneously to the much slower motions of the nuclei. As the nuclei move through a position $\mathbf{R}$, the electrons readjust to the same optimum configuration that they would have if the nuclei were stationary at position $\mathbf{R}$. The energy of this optimal electronic configuration is $\mathscr{E}(\mathbf{R})$, a point on the potential-energy surface. Knowledge of $\mathscr{E}(\mathbf{R})$ is sufficient to determine structure and reactivity; explicit knowledge of electronic motion is not required once $\mathscr{E}(\mathbf{R})$ has been determined.

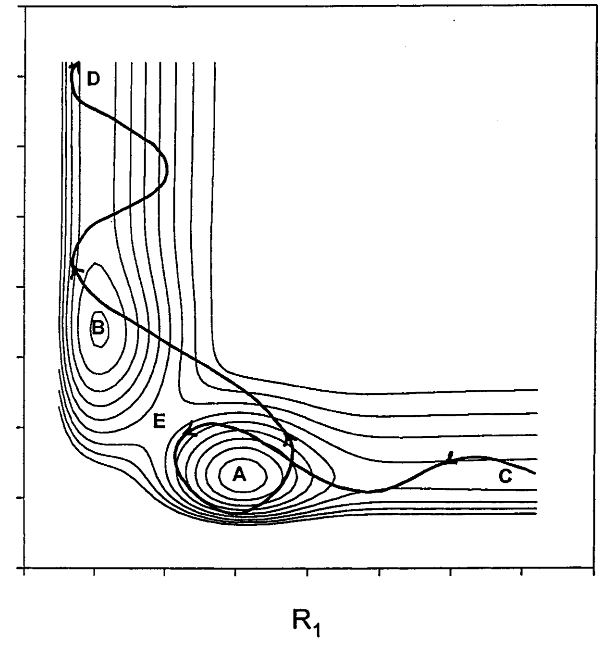

Fig. 1. A schematic two-dimensional representation of a multidimensional potential-energy surface. R_1 and R_2 represent bond distances. The *solid curves* are contours of equal electronic energy, $\mathscr{E}(\mathbf{R})$

This prompted Eyring and Polanyi [2], in 1931, to present the first formulation of chemical reaction dynamics in terms of a multidimensional potential-energy surface, using the hydrogen-exchange reaction as an example. The electrons have not been removed from the problem, of course. For any nuclear configuration $\mathbf{R}$, the energy $\mathscr{E}(\mathbf{R})$ is determined by the full, many-electron Schrödinger equation for fixed nuclear positions $\mathbf{R}$. Thus, the Born-Oppenheimer approximation separates the problem of chemical structure and reactivity into two parts: the electronic structure part and the nuclear motion part.

The Born–Oppenheimer separation is derived as follows. The total nonrelativistic quantum mechanical Hamiltonian for a system of interacting atoms is

$$\begin{aligned}\mathscr{H} &= -\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla^2_{\mathrm{R}_\alpha} - \frac{\hbar^2}{2}\sum_i m_\mathrm{e}^{-1}\nabla^2_\mathrm{r} + V(\mathbf{r},\mathbf{R}) \\ &= -\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla^2_{\mathrm{R}_\alpha} + \mathscr{H}_\mathrm{el}(\mathbf{r};\mathbf{R}) \ , \end{aligned} \tag{1}$$

where $\mathbf{r}$ and $\mathbf{R}$ denote the positions of the electrons and nuclei, respectively, M_α is the mass of nucleus α and m_e is the electron mass. $V(\mathbf{r},\mathbf{R})$ includes all interparticle interactions: electron–electron repulsions, electron–nuclear attractions, and nuclear–nuclear repulsions. Thus $\mathscr{H}_\mathrm{el}(\mathbf{r};\mathbf{R})$ is the entire Hamiltonian of the system with the exception of the kinetic-energy operator for the slow particles. $\mathscr{H}_\mathrm{el}(\mathbf{r};\mathbf{R})$ can be viewed as the Hamiltonian that governs the electrons when the nuclei are fixed at position $\mathbf{R}$. We now define the adiabatic (Born–Oppenheimer) electronic wave functions $\Phi_j(\mathbf{r};\mathbf{R})$ to be the eigenfunctions of $\mathscr{H}_\mathrm{el}(\mathbf{r};\mathbf{R})$ for a fixed $\mathbf{R}$:

$$\mathscr{H}_\mathrm{el}(\mathbf{r};\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R}) = \mathscr{E}_j(\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R}) \ . \tag{2}$$

$\mathscr{E}_j(\mathbf{R})$ is the adiabatic or Born-Oppenheimer potential-energy surface corresponding to electronic state j. The ground-state ($j = 0$) potential-energy surface $\mathscr{E}_0(\mathbf{R})$ is the same as that referred to in qualitative terms in the first paragraph. The $\mathscr{E}_j(\mathbf{R})$ for $j \neq 0$ are the potential-energy surfaces corresponding to the excited electronic states. The $\Phi_j(\mathbf{r};\mathbf{R})$ depend only parametrically on the nuclear positions $\mathbf{R}$; thus the semicolon in $\Phi_j(\mathbf{r};\mathbf{R})$. The ground- and excited-state electronic wave functions $\Phi_j(\mathbf{r};\mathbf{R})$, for any fixed $\mathbf{R}$, constitute a complete set that spans the space of the electrons; thus, we can express the exact molecular wave function $\Psi(\mathbf{r},\mathbf{R})$ as

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_i \Phi_i(\mathbf{r};\mathbf{R})\Omega_i(\mathbf{R}) \ . \tag{3}$$

Substituting Eq. (3) into the Schrödinger equation using the Hamiltonian of Eq. (1), multiplying from the left by $\Phi_j^*(\mathbf{r};\mathbf{R})$, and integrating over electronic coordinates $\mathbf{r}$, we obtain a set of coupled Schrödinger equations for the wave functions $\Omega_j(\mathbf{R})$ describing nuclear motion on each potential-energy surface, $\mathscr{E}_j(\mathbf{R})$:

$$\begin{aligned}&-\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla^2{}_{\mathrm{R}_\alpha}\Omega_j(\mathbf{R}) + \mathscr{E}_j(\mathbf{R})\Omega_j(\mathbf{R}) - E\Omega_j(\mathbf{R}) \\ &\quad = -\frac{\hbar^2}{2}\sum_i D_{ji}(\mathbf{R})\Omega_i(\mathbf{R}) + \hbar^2\sum_{i\neq j}\mathbf{d}_{ji}(\mathbf{R})\cdot\nabla_{\mathrm{R}_\alpha}\Omega_i(\mathbf{R}) \ , \end{aligned} \tag{4}$$

where the first and second derivative matrix elements are defined as

$$\mathbf{d}_{ij}(\mathbf{R}) = -\sum_\alpha M_\alpha^{-1}\int\left\{\Phi_i^*(\mathbf{r},\mathbf{R})\left[\nabla_{\mathrm{R}_\alpha}\Phi_j(\mathbf{r},\mathbf{R})\right]\right\}\mathrm{d}\mathbf{r} \ , \tag{5}$$

$$\mathrm{D}_{ij}(\mathbf{R}) = -\sum_\alpha M_\alpha^{-1}\int\left\{\Phi_i^*(\mathbf{r},\mathbf{R})\left[\nabla^2_{\mathrm{R}_\alpha}\Phi_j(\mathbf{r},\mathbf{R})\right]\right\}\mathrm{d}\mathbf{r} \ . \tag{6}$$

By neglecting the right-hand side of Eq. (4), we obtain

$$\left[-\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla^2_{\mathrm{R}_\alpha} + \mathscr{E}_j(\mathbf{R}) - E\right]\Omega_j(\mathbf{R},t) = 0 \ . \tag{7}$$

Note that the first term on the right-hand side of Eq. (4) contains a diagonal term involving $D_{jj}(\mathbf{R})$. This term is frequently included in Eq. (7) as a correction to $\mathscr{E}_j(\mathbf{R})$. We omit it here for simplicity; it is of the same order of magnitude as the neglected off-diagonal $D_{ij}(\mathbf{R})$ terms. The final result, Eq. (7), is that nuclear motion is governed by a Schrödinger equation, with the potential-energy function given by $\mathscr{E}_j(\mathbf{R})$. $\mathscr{E}_j(\mathbf{R})$, in turn, is obtained from Eq. (2) for each required nuclear geometry $\mathbf{R}$. This is the Born-Oppenheimer approximation.

Born and Oppenheimer presented the theoretical justification for neglecting the two terms on the right-hand side of Eq. (4) using perturbation theory, with the small parameter ξ chosen to be

$$\xi = (m_\mathrm{e}/M)^{1/4} \ . \tag{8}$$

M is a typical nuclear mass and m_e is the electron mass, taken to be unity. For a diatomic molecule vibrating near its minimum, the internuclear separation is expressed as

$$R = R_0 + \xi u \ . \tag{9}$$

where the reduced distance u was argued to be of order unity, i.e., of the same order as R_0. From Eqs. (8) and (9), $M^{-1} \propto \xi^4$ and $\partial/\partial R \propto \xi^{-1}$. This gives the following scaling relationships:

$$\text{Typical vibrational energy} \propto 1/\sqrt{M} \propto \xi^2 \ ,$$

$$\text{Typical rotational energy} \propto 1/MR_0^2 \propto \xi^4 \ ,$$

$$\text{First derivative coupling} \propto \mathbf{d}_{ij}(\mathbf{R})\partial/\partial R \propto M^{-1}\partial/\partial R \propto \xi^3 \ ,$$

$$\text{Second derivative coupling} \propto D_{ij}(\mathbf{R}) \propto M^{-1} \propto \xi^4 \ .$$

For M of order $10^4 m_e$, ξ is of order 0.1. Thus, typical vibrational and rotational energies are of order 10^{-2} and 10^{-4}, respectively, compared to electronic energies. The $D_{jj}(\mathbf{R})$ correction to the potential-energy surface $\mathscr{E}_j(\mathbf{R})$ is of order 10^{-4}, similar to a rotational spacing. The mixing of electronic states $i \neq j$ is proportional to the squares of the first and second derivative couplings, i.e., $\xi^6 \approx 10^{-6}$ and $\xi^8 \approx 10^{-8}$, respectively. This provides the justification for the Born-Oppenheimer approximation.

The impact of the Born-Oppenheimer approximation in chemistry is pervasive. It is not an exaggeration to say that the single activity that has demanded the most effort (both intellectual and computational) from theoretical chemists in the twentieth century is the electronic structure problem, i.e., the calculation of $\mathscr{E}_j(\mathbf{R})$ for fixed $\mathbf{R}$ by ab initio, semiempirical, and empirical approaches. The tremendous improvements in the accuracy and practicality of ab initio methods that have been achieved were recognized by the award of the 1998 Nobel Prize in Chemistry to Walter Kohn and John Pople. Electronic structure computer codes have now become an invaluable tool of the modern theoretical and experimental chemist. This tool is applied routinely to elucidate structure and reactivity in a myriad of ways. With the help of methods for computing analytical derivatives, local minima of $\mathscr{E}_j(\mathbf{R})$ can be found and characterized. This directly gives the structure and stability of bound molecular species. In addition, analytical second derivatives of $\mathscr{E}_j(\mathbf{R})$ provide the force constants needed to compute vibrational spectra. Electronic spectra can be computed from the energy spacings of $\mathscr{E}_j(\mathbf{R})$ for different electronic states j, combined with the overlap integrals between vibrational wave functions computed on the two potential surfaces. The latter, called "Franck-Condon factors" were described in the original Born-Oppenheimer paper. Many other properties can be computed from the fixed-nuclei electronic wave functions, including spin-orbit interactions, magnetic resonance chemical shifts, molecular polarizabilities, dipole moments and transition dipoles, ionization potentials and electron affinities, etc. Analytical first and second derivatives of $\mathscr{E}_j(\mathbf{R})$ also facilitate the location and characterization of transition states, allowing ab initio determination of chemical reaction rates using transition-state theory. Monte Carlo sampling of the potential-energy surface has become a practical method in statistical mechanics for obtaining thermodynamic properties of molecules, fluids, adsorbates on surfaces, etc.

The Born-Oppenheimer approximation is also the cornerstone of the field of chemical dynamics. "Molecular dynamics", the simulation of the classical mechanical motion of interacting atoms, has important applications in fields ranging from biology to materials engineering. Molecular dynamics is based on, first, the Born–Oppenheimer approximation, and second, the classical limit of Eq. (7). The latter requires calculation of the classical forces, i.e., derivatives of $\mathscr{E}_j(\mathbf{R})$. This can be done either in advance or point-by-point along the trajectory, employing ab initio, semiempirical, or empirical methods. For all these alternatives, the nuclei evolve via classical mechanical equations of motion on an approximation to the Born-Oppenheimer potential-energy surface $\mathscr{E}_j(\mathbf{R})$, of Eq. (2). Thus, the terminology "quantum molecular dynamics" that is sometimes applied when ab initio forces are used is unfortunate. This classification should be reserved for situations where the heavy-particle motion is treated by quantum mechanics, i.e., Eq. (7).

Central to the argument of Born and Oppenheimer is the assumption that electronic wave functions vary on a spatial scale comparable to the reduced distance u of Eq. (9), i.e.,

$$\int \{\Phi_i^*(\mathbf{r}, u)[\partial\Phi_j(\mathbf{r}, u)/\partial u]\}\mathrm{d}\mathbf{r} \approx 1 \ . \tag{10}$$

This condition is not always satisfied. For example, in regions where two electronic states approach very closely in energy, the adiabatic electronic wave functions can change significantly in character in response to a very small change internuclear distance. For such "avoided-crossing" situations, the Born-Oppenheimer approximation may be invalid [3]. There are many such situations in chemistry. Examples include nonradiative transitions in molecules and solids, electron transfer, quenching of excited electronic states, collisional electronic excitation, and inelastic electron scattering. To describe such processes, "nonadiabatic transitions" among different potential-energy surfaces must be accounted for; however, this language is still based on the Born–Oppenheimer concept of potential-energy surfaces. Thus, the Born-Oppenheimer separation of electronic and nuclear motion remains central to the description, but the theory must be extended to multiple electronic states. This requires calculation of the derivative coupling matrix elements of Eqs. (5) and (6), an area where further progress is required.

Another area that will draw attention in the future is "true" quantum molecular dynamics, in which Eq. (7) or its time-dependent form describing the nuclear motion is solved quantum mechanically, without the classical approximation. This represents the ultimate limit of the Born-Oppenheimer approximation. In some cases it may be advantageous to make an additional, second-level Born-Oppenheimer separation of fast and slow nuclear motions, with inclusion of nonadiabatic transitions among nuclear quantum states.

While quantum mechanical simulation of nuclear motion will become more practical in the future, classical mechanical molecular dynamics will remain an important tool for simulating large molecular systems for many years to come. Ab initio determination of forces will play an increasingly large role. But a system of N atoms requires at least $10^{3\mathrm{N}}$ points to completely map out $\mathscr{E}_j(\mathbf{R})$ (ten points along each degree of freedom). For N of order 100, it is clearly prohibitive to comprehensively tabulate $\mathscr{E}_j(\mathbf{R})$ in advance (in the absence of simplifications such as pairwise additivity). By contrast, a l-ns trajectory with l-fs time steps requires 10^6 evaluations of $\mathscr{E}_j(\mathbf{R})$ and its derivatives, a very formidable task but far more accessible than the alternative. Thus, it will be essential in the future to develop "on-the-fly" methods for ab initio calculation of forces [4].

The Born-Oppenheimer approximation separates the theoretical study of molecules into two parts, the electronic structure part, Eq. (2), and the nuclear motion part, Eq. (7). This has produced a separation among theoretical chemists themselves: the electronic structure theorists and the statistical mechanics/dynamics theorists, i.e., those that compute $\mathscr{E}_j(\mathbf{R})$ and those that use it. While this is an overstatement and there have been many theorists with a foot in each camp, this bifurcation has been unhealthy for chemistry. Theoretical chemists of the future will need to be expert in both electronic structure and statistical mechanics/dynamics (perhaps as well as in biology, condensed matter physics, materials science, environmental science, computer science, ...?).

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