

The Born-Oppenheimer approximation and its role in the reduction of chemistry

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1. The reduction of chemistry to quantum mechanics

Perhaps the main question in the field of philosophy of chemistry has been whether chemistry reduces to quantum mechanics. The reason for this state of affairs is the simple fact that if chemistry does indeed reduce to quantum mechanics, then chemistry can be regarded as a sub-branch of quantum physics with no relevant philosophical questions. Moreover, the reduction of chemistry to quantum mechanics was regarded as a paradigmatic case of successful reduction in the time that logical positivism was the accepted view of the nature of science. Needless to say, the pioneers of the philosophy of chemistry have generally argued that chemistry does not in fact reduce to quantum mechanics and that it has its own interesting philosophical problems that are worthy of pursuing (Van Brakel, 2000).

There are many ways that the question of reduction has been explored in the philosophical literature. First of all, Nagel's criteria for reduction (Nagel, 1961) have been applied, namely attempts to axiomatize the theory to be reduced as well as the more fundamental theory, followed by the attempt to establish bridge principles (Hettinger, 2012). These attempts are generally considered to fail in the case of chemical theories because it is not clear what an axiomatization of chemical theories might consist of.

More naturalistic approaches which move beyond the formal Nagelian approach have examined the calculations that are used in quantum chemistry in an attempt to establish whether the measured properties of atoms and molecules can be calculated in a truly *ab initio* fashion. However, even if a computational gap remains between what quantum mechanics is capable of predicting as compared with measurable chemical properties, the more general question of whether chemistry can be reduced in principle rather than in practice remains. Such metaphysical investigations have sought to examine the nature of emergence, causation and laws in chemistry (Lombardi, Labarca, 2005, Hendry, 2010; Seifert, 2023)

Quantum chemistry, and general chemistry, traditionally use the concept of atomic orbitals in order to explain many chemical phenomena. Here the philosophical issue has centered

on whether atomic orbitals genuinely reduce to quantum mechanics (Scerri 1991). Such discussions were greatly enlivened starting in 1999 when it was reported that atomic orbitals had been experimentally observed for the first time (Mulder 2010).

More recently the question of reduction has centered around the nature of the Born-Oppenheimer approximation or BOA, which widely used in calculations involving molecules, and which is the main focus of the present article.

2. Born Oppenheimer approximation (BOA)

The BOA is very frequently applied in theoretical chemistry in order to solve the Schrödinger equation for any particular molecule. Several prominent philosophers have claimed that the use of this approximation represents a violation of the Heisenberg Uncertainty Principle and that this feature implies that chemistry does not reduce to quantum mechanics (Chang, 2015; Cartwright, 2022; Lombardi, 2013, 2023) These same authors also claim that chemists have no choice but to use this approximation in order to solve the appropriate Schrödinger equation for each system. Here I will argue that both of these claims are mistaken, by examining the nature of the BOA and the more general Born-Huang (B-H) representation.

For example, in a recent book, Nancy Cartwright writes,

The typical method of quantum-mechanical treatment of molecules begins with the Born–Oppenheimer approximation, which separates out the nuclear wavefunction from the electronic wavefunction ($\Psi_{\text{total}} = \Psi_{\text{nuclear}} \times \Psi_{\text{electronic}}$). Additionally, it is assumed that the nuclei have fixed positions in space (Cartwright, 2022)

But this fundamentally violates quantum mechanics which, following the Heisenberg uncertainty principle, maintains that we cannot have a simultaneous assignment of fixed positions and fixed momenta (Cartwright, 2022).

Hasok Chang has written,

First, as R. Guy Woolley among others have observed for many years (Sutcliffe and Woolley 2012, and references therein), the typical method of quantum-mechanical

treatment of molecules begins with the Born–Oppenheimer approximation, which separates out the nuclear wavefunction from the electronic wavefunction ($\Psi_{\text{total}} = \Psi_{\text{nuclear}} \times \Psi_{\text{electronic}}$). Additionally, it is assumed that the nuclei have fixed positions in space. In this “clamping-down” approximation, the atomic nuclei are treated essentially as classical particles; as Olimpia Lombardi (2013) points out, this picture is non-quantum in a very fundamental way as the simultaneous assignment of fixed positions and fixed momenta (namely, zero) to them violates the Heisenberg uncertainty principle. But without such classical scene-setting, the quantum calculations are quite impossible (Chang, 2015).

More recently Lombardi, whom Chang cites above, has written,

The BOA, as used in the context of quantum chemistry, is a vivid example of how scientists “outrageously” appeal to incompatible theories in their practice. In this case, quantum chemical models of molecules are obtained by combining classical mechanics to describe the nuclei and quantum mechanics to account for the motion of the electrons. As explained, such a combination is not an innocent strategy that could be circumvented if we had access to a higher level of calculating power (Lombardi, 2023, 15).

3. The application of the BOA to the H_2^+ ion-molecule

The simplest of all molecules, or strictly speaking the simplest ion consisting of two bound nuclei, is the H_2^+ system, which will be used to begin an analysis of how the Born-Oppenheimer is used in quantum mechanical calculations.

As is well-known, central equation in quantum mechanics, is the time independent Schrödinger equation, as shown in its most compact below in equation (1).

$$H \Psi = E \Psi \quad (1)$$

It consists of a Hamiltonian operator, H , which acts on the wavefunction for the system Ψ and thereby yields an infinite set of possible discrete energy values denoted by the eigenvalues, E . The Hamiltonian itself contains operators specifying the kinetic and potential energies of every

particle in the system. In the case of the H_2^+ system there are two protons and just one electron. Consequently, there are two kinetic energy terms, one for each of the protons, in addition to a potential energy term due to their mutual repulsion. In the case of the electron there is a kinetic energy term and two potential energy terms, for the attraction between the electron and each of the protons. The mathematical expression for the Schrödinger equation in which the Hamiltonian is shown explicitly is,

$$\left[-\frac{1}{2} M \nabla_A^2 - \frac{1}{2} M \nabla_B^2 + \frac{e \cdot e}{R_{AB}} - \frac{1}{2} m \nabla^2 - \frac{e \cdot e}{r_A} - \frac{e \cdot e}{r_B} \right] \Psi = E \Psi \quad (2)$$

where ∇ is the Laplacian differential operator, M and m are the masses of the proton and the electron respectively, R_{AB} the distance between the protons, r_A and r_B the distance of the electron from each of the nuclei A and B and e is the charge on the electron.

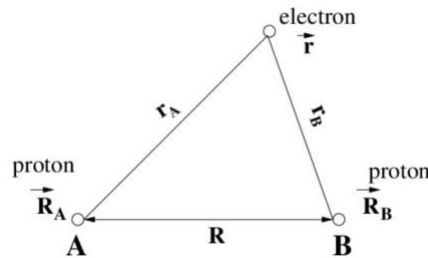


Figure 1. The H_2^+ system consisting of two protons and one electron.

The application of the Born-Oppenheimer approximation consists in recognizing that electrons are so much lighter than protons, or more specifically, $9.1093819 \times 10^{-31}$ kg as compared with $1.6726216 \times 10^{-27}$ kg, or a ratio of 1 to 1836. If one assumes that an equal momentum is given to a proton and an electron, and if M and m are the masses of the proton and the electron respectively,

$$\begin{aligned} \text{Momentum} &= M v_{\text{proton}} = m v_{\text{electron}} \\ &= 1836 \times v_{\text{proton}} = 1 \times v_{\text{electron}} \\ v_{\text{electron}} / v_{\text{proton}} &= 1836 / 1 \end{aligned}$$

The relative speeds of the electron and the proton are therefore 1836 to 1 in favor of the electron. According to the popular interpretation of BOA, this discrepancy in velocities is taken to the limit, in that protons are assumed to have a velocity of zero as compared to that of electrons. It follows that their kinetic energies ($1/2 mv^2$) will also be zero. Consequently, most textbooks state that all kinetic energy terms for protons can be neglected under the BOA scheme and equation 2, therefore reduces to equation (3).

$$\left[+ \frac{e \cdot e}{R_{AB}} - \frac{1}{2} m \nabla^2 - \frac{e \cdot e}{r_A} - \frac{e \cdot e}{r_B} \right] \Psi = E \Psi \quad (3)$$

Furthermore, the first term in (3) takes on a constant value for any particular fixed inter-proton distance. What remains is therefore three operators, all referring to the electron, which operate on the wavefunction to determine the allowed eigenvalues for the system. Such an equation does not involve any electron-electron repulsion terms, since there is only one electron present, and the equation can therefore be solved analytically, meaning exactly.

The result computed in this way for the ground state energy of the H_2^+ system is – 0.602342 Hartrees, as compared with the experimentally obtained value of –0.596689 Hartrees, or a difference of approximately 1%. Clearly the BOA appears to be justifiable for this system, at least in numerical terms. Moreover, the error decreases when one considers molecules with heavier nuclei. For example, in the case of the C_2 molecule, the nuclei concerned are twelve times as heavy as the proton which means that the error will be reduced to at least $1/12^{\text{th}}$ of the value for the H_2^+ system.

So much for the elementary or typical textbook treatment of the BOA. Let us now return to what some philosophers of science, as well as some philosophers of chemistry, have made of this situation. In what is perhaps a more extreme position, as seen in the opening quotations, some authors claim that the use of the BOA results in a treatment of particles in a fundamentally non-quantum manner, because fixed positions are assigned to the nuclei and that this step represents a violation of the Heisenberg Principle. These same authors frequently go on to claim that without such classical “scene setting” the quantum calculations are quite impossible, as also seen in the above quotations.

My first objection to this claim is of a very broad nature. The notion that denying any motion to nuclei in a molecule represents a violation of the Heisenberg Principle ignores the fact

that scientific theories frequently contain internal inconsistencies. Stated otherwise, scientific progress is not restricted by matters of principle. Numerous instances from the history of science can be used to show that progress was achieved by violating what may hitherto have seemed to be inviolable restrictions. For example, the Bohr model contains several apparent inconsistencies and yet it represented a major step forward and the beginnings of the quantum theory of atoms, which culminated in the discovery of quantum mechanics (Vickers 2013).

What matters more in scientific practice is obtaining a result. If an approximation provides a calculation that falls short of the experimental value by 1%, or less for heavier systems, it is considered perfectly reasonable, even if it may appear to violate a central principle of the theory that is being utilized.

One can point to other apparent violation of fundamental principles the practice of atomic and molecular physics and chemistry. For example, the use of electronic configurations of atoms, that are ubiquitous in chemistry and physics, and which specify which electrons are in which particular orbitals, represents a violation of the Pauli Principle, which asserts that electrons are completely indistinguishable. And yet electronic configurations are routinely and successfully used in chemical reasoning as well as calculations (Scerri, 1991). So even if the BOA did represent a violation of the Uncertainty Principle I do not believe that this would have such a negative impact on the claim that chemistry is reduced to quantum mechanics. But as later sections will argue, there is in fact no such violation of the principle.

4. Does BOA represent a violation of Heisenberg's Principle?

In addition to the general points mentioned in the previous section, there is a significant sense in which the use of the BOA does *not* in fact represent a violation of the Heisenberg Principle. Solving equation (3) above involves obtaining many solutions for the total electronic energy, one for each particular chosen internuclear distance. It is only by doing so that a graph of the potential energy of the nuclei can be plotted against distance (Figure 2), in order to obtain the minimum in the plot and thereby the ground state energy and bond length of the system in question. In other words, even though each particular solution may seem to keep the nuclei stationary, the fact that one is considering many different inter-nuclear distances serves to restore the motion of nuclei. The Heisenberg Principle might only be said to be violated if one were to focus on just a single data point on the energy graph shown below.

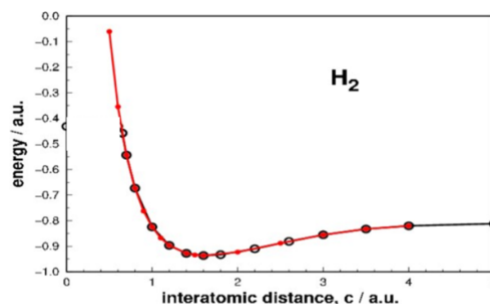


Figure 2. Potential energy of nuclei against inter-nuclear distance.

Another point to emerge from some of the views cited above is the notion that quantum chemists are somehow obliged to use the BOA. In fact, there has long existed a thriving branch of quantum chemistry which specializes in non-Born-Oppenheimer calculations (Agostini and Curchod 2022). Such calculations have a wide variety of applications in chemistry such as the interaction between light and matter and ultrafast, out-of-equilibrium nuclear dynamics. This work includes the photochemistry of isolated and solvated molecules and excited-state dynamics with long timescales and will be briefly considered in a section below.

5. Another view of the Born-Oppenheimer approximation

Another way to understand the implications of the BOA more clearly is to realize that it does not in fact consist of simply setting the kinetic energy to zero although it is frequently represented as such.¹

Born and Oppenheimer focused on the electronic part of the molecular wavefunction that can be solved within the time independent Schrödinger equation for the electrons in a molecule. They showed that for a given nuclear configuration the electronic wavefunction provides a complete basis for the electronic states. If this process is now repeated for any nuclear configuration, one obtains a basis set of electronic states that connects any possible nuclear configuration. This is the process that Born and Oppenheimer used to express the molecular wavefunction in terms of a single product of the electronic wavefunction, that is defined by the time-independent electronic wavefunction and a nuclear wavefunction.

It is this single product representation which is the true essence of the BOA and not the setting of kinetic energy to zero. To repeat, the BOA approximation consists in supposing that the molecular wavefunction can only be expressed as a single product of the nuclear

wavefunctions for the system and the electronic wavefunction that is a solution of the time-independent Schrödinger equation. The consequence of making this assumption is that the nuclei are forced to remain in single eigen states. Moreover, this situation is equivalent to the statement made above that the nuclei are much heavier than the electrons, so much so that the electrons adapt instantaneously to any nuclear motion. It does not mean that the nuclei are in fact clamped.

It is worth realizing that if nuclei were clamped the result would be that no chemistry would ever be possible, since chemical reactions invariably require the nuclei of atoms to move towards each other before interacting to form products. As one chemist has stated, the notion of clamping nuclei is completely orthogonal to what occurs in chemistry, namely the coming together of nuclei and indeed entire atoms in order for them to react.²

6. The Born-Oppenheimer approximation for any many-electron system.

The analysis of the BOA given in an earlier section was examined in the context of a one electron system, namely the H_2^+ ion. In the present section we consider how the approximation applies to any many-electron molecule.

$$\hat{H} = -\sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \nabla_{\gamma}^2 - \sum_i \frac{\hbar^2}{2} \nabla_i^2 + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{\gamma, i} \frac{Z_{\gamma}}{|\mathbf{R}_{\gamma} - \mathbf{r}_i|} + \sum_{\gamma < \beta} \frac{Z_{\gamma} Z_{\beta}}{|\mathbf{R}_{\gamma} - \mathbf{R}_{\beta}|} \quad (3)$$

This expression differs from equation 2 above in that it includes a term for electron-electron repulsions (the 3rd term on the right side), which was absent in the one electron case for H_2^+ . The absence of the electronic charge e in equation 3 is due to the use of atomic units for which $e = 1$ and the mass of the electron = 1. The \hbar is retained for the sake of clarity, even though it too is equal to one in atomic units. The expression can be simplified by collecting together all the terms which refer to the electrons, namely all but the first one on the right-hand side, as the Hamiltonian operator for the electrons,

$$= -\sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \nabla_{\gamma}^2 + \hat{H}_{el} \quad (4)$$

This molecular wave function therefore describes both the nuclei and the electrons. In the BOA the nuclear kinetic energy term, or the first term on the right-hand side in equations 3 and 4, is very small, given the large mass of the nuclei M as compared with the masses of the electrons. This nuclear kinetic energy operator can therefore be considered as a small perturbation. It is worth noting that this is not being set to zero in this more rigorous version and that one should not conclude that the nuclei have been clamped. Within this approximation the eigenstates and eigenvalues can be calculated by solving the time-independent Schrödinger equation for the electronic motion.

This BOA as first proposed in 1927 consists of first separating the total wavefunction into separate nuclear and electronic contributions and secondly in assuming that the nuclear and electronic motions can be decoupled (Born, Oppenheimer, 1927). If one assumes counterfactually that the nuclear mass is infinite one can then allow the kinetic energy of the nuclei to tend to zero as an approximation and as a result the nuclear positions are no longer dynamical variables in the Hamiltonian but are merely parameters.³ The parametric dependence is symbolized by writing “; \mathbf{R} ”.

Having fixed the nuclear degrees of freedom in a given configuration one can then solve the electronic Schrödinger equation for this fixed set of nuclear positions. This process can then be repeated any number of times in order to obtain a potential energy surface by analogy with the potential energy curve that was obtained for the one electron system as shown in figure 2.

In mathematical terms the Schrödinger equation expressions become,

$$\begin{aligned} \left[\hat{T}_e + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) \right] \Phi_I(\mathbf{r}; \mathbf{R}) &= E_I^{el}(\mathbf{R})\Phi_I(\mathbf{r}; \mathbf{R}) \\ \hat{H}_{el}\Phi_I(\mathbf{r}; \mathbf{R}) &= E_I^{el}(\mathbf{R})\Phi_I(\mathbf{r}; \mathbf{R}) \end{aligned} \quad (5)$$

Solving this time-independent Schrödinger equation provides the electronic states in the adiabatic representation. The solutions of this equation form a complete basis in the Hilbert space of the electronic wavefunctions. It follows that one can expand the many-electron wavefunction as a linear combination of the eigenvectors, expressed as,

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_J^{\infty} \Phi_J(\mathbf{r}; \mathbf{R}) \chi_J(\mathbf{R}, t) \quad (6)$$

where the J 's are labels for the electronic states and $\Phi_J(\mathbf{r}; \mathbf{R})$ are the electronic wavefunctions and the coefficients $\chi_J(\mathbf{R}, t)$ are related to the nuclear wavefunctions in each electronic state.

This equation 6 is known as the Born-Huang representation of the molecular wavefunction and it is formally exact.

7. The Born – Huang generalization of BOA

Although the BOA was first proposed and put to work in 1927, the starting point to the modern approach to BOA consists of the more general Born-Huang (B-H) representation as expressed in equation 6. This more recent formulation dates from the appendix of a book by Born and his student Huang in 1954, and it allows one to gain a more fundamental understanding about the nature of the original B-O approach which, as it emerges, is a particular instance of B-H (Born, Hunag, 1954, Tully, 2000).

Whereas the BOA is only concerned with the ground state wavefunction of any particular molecule, the B-H approximation considers all excited state wavefunctions in addition to that of the ground state. In the B-H framework the sum of all these wavefunctions provides an exact solution to the Schrödinger equation for the system and it can be shown in a more rigorous manner that the naïve notion that the BOA demands that all nuclei be stationary is incorrect.

The terms that are neglected in the BOA are those that couple nuclear motion to the motion of the electrons with the change of electronic states. In this more general B-H framework it is clear that the nuclei move, even if they do so only slowly, so that in many cases the electrons can adapt quickly to such changes. In the terminology of quantum mechanics, the electrons adapt adiabatically to the nuclear motion, in that they remain in the same eigen state. This is an example of the general quantum mechanical principle called the adiabatic theorem. It states that if one has a wavefunction that depends on parameters that can change then, provided that they are changed slowly, the wavefunction always remains in a given eigenstate.

However, if the nuclei move rapidly this is no longer the case. The B-H description of the molecular wavefunction makes precisely this statement. If the nuclei move quickly, which is what occurs in photochemical reactions and other ultra-fast chemical processes, the electrons experience a moment of ‘confusion’ and the motion of the nuclei results in a change in the eigenstate. Such a situation constitutes a non-B.O effect, which can be successfully tackled through numerous mathematical approaches have been developed for this purpose (Nikitin, 1999; Hammes-Schiffer et al., 2008; Xu et al., 2022).⁴

Within the BOA one limits oneself to just one term in the B-H representation, which means that the nuclear degrees of freedom can only evolve on a single electronic eigenstate. This limitation is removed when one turns to the B-H representation. The situation can be expressed formally as follows,

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum \Phi_J(\mathbf{r}; \mathbf{R}) \chi_J(\mathbf{R}, t)$$

Born-Oppenheimer

$$\Psi(\mathbf{r}, \mathbf{R}, t) \xrightarrow[\text{Huang}]{\text{Born-}} \sum_J^{\infty} \Phi_J(\mathbf{r}; \mathbf{R}) \chi_J(\mathbf{R}, t)$$

The difference is that the BOA, unlike the B-H representation, does not involve a summation over different electronic eigenstates.

8. Non-B.O calculations in contemporary chemistry

Finally, the notion that quantum chemists are obliged to use the BOA, as expressed by various authors including the example below is incorrect,

The BOA introduces molecular features that are conceptually alien to the quantum description. Therefore, it is a strategy completely unacceptable from the viewpoint of scientific realism, and it only makes sense from a pragmatic realist perspective (Lombardi, 2023).

There are literally thousands of studies that go beyond the BOA in a sub-discipline that concerns itself with non-Born-Oppenheimer calculations. Such calculations have widespread applications throughout contemporary chemistry. For example, the BOA is only applicable to the ground states of molecules. Much research in areas such as photochemistry requires an analysis of the excited states of molecules. Such analyses are carried out routinely by considering the coupling of nuclear and electronic motion or, stated otherwise, by considering a non-adiabatic situation in which the motion of the nuclei does influence that of the electrons in a molecule. In such a case the electronic motion does not readjust itself instantaneously when the nuclei move.

In order to obtain information concerning the nuclear dynamics, something that is completely ignored in the BOA, the B-H representation,

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_J \Phi_J(\mathbf{r}; \mathbf{R}) \chi_J(\mathbf{R}, t)$$

is inserted into the time dependent Schrodinger equation,

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \hat{H} \Psi(\mathbf{r}, \mathbf{R}, t).$$

to give,

$$i\hbar \frac{\partial}{\partial t} \sum_I \Phi_I(\mathbf{r}; \mathbf{R}) \chi_I(\mathbf{R}, t) = \hat{H} \sum_I \Phi_I(\mathbf{r}; \mathbf{R}) \chi_I(\mathbf{R}, t).$$

The next step consists of multiplying each side on the left by the complex conjugate of the wavefunction,

$$i\hbar \frac{\partial}{\partial t} \sum_J \chi_J(\mathbf{R}, t) \int d\mathbf{r} \Phi_I^*(\mathbf{r}; \mathbf{R}) \Phi_J(\mathbf{r}; \mathbf{R}) = \sum_J \int d\mathbf{r} \Phi_I^*(\mathbf{r}; \mathbf{R}) \hat{H} \Phi_J(\mathbf{r}; \mathbf{R}) \chi_J(\mathbf{R}, t).$$

Due to the orthonormality of the electronic basis set this can be rewritten as,

$$i\hbar \frac{\partial}{\partial t} \chi_I(\mathbf{R}, t) = \left[- \sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \nabla_{\gamma}^2 + E_I^{el}(\mathbf{R}) \right] \chi_I(\mathbf{R}, t) + \sum_J C_{IJ} \chi_J(\mathbf{R}, t)$$

This expression represents the time dependent nuclear wavefunction for each electronic state, in which $C_{IJ}(\mathbf{R})$ is a non-adiabatic coupling term and $E_I^{el}(\mathbf{R})$ provides the potential energy surface for the nuclei in the electronic state I.

Provided that the molecule evolves on a given electronic states sufficiently far away from other higher energy electronic states, the coupling term can be ignored, and we return to the adiabatic BOA equation of,

$$i\hbar \frac{\partial}{\partial t} \chi_I(\mathbf{R}, t) = \left[- \sum_{\gamma} \frac{\hbar^2}{2M_{\gamma}} \nabla_{\gamma}^2 + E_I^{el}(\mathbf{R}) \right] \chi_I(\mathbf{R}, t)$$

It is important to note that the first term on the right-hand side is not set to zero, which means that the nuclear kinetic energy is not equal to zero, which once again emphasizes that the nuclei are not clamped.

But if the coupling terms are included it becomes possible to treat systems such as the H_5O_2^+ ion, which is the simplest model of a hydrated proton. A simulation of this so-called Zundel cation requires a quantum treatment of the five hydrogen nuclei in their full dimensionality of 15 degrees of nuclear freedom.

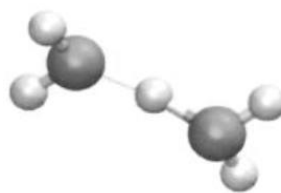


Figure 3. The H_5O_2^+ or Zundel ion.

A calculation of the potential energy surface, and through it the of the infra-red predissociation spectrum of the system, shows excellent agreement with the experimental spectrum as can be seen in figure 4.

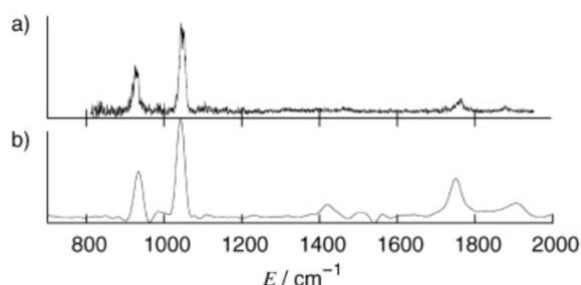


Figure 4. Comparison of the experimental spectrum (a) and the calculated predissociation spectrum of the H_5O_2^+ ion (b) (Vendrell et al, 2007)

Conclusions

Contrary to the statements found in the philosophy of science literature, and even some chemistry textbooks, the BOA does not imply literally clamping the nuclei in a molecule. Nuclear motion is always coupled to the motion of the electrons. In cases where one only considers the ground state of a molecule, and if the energies of the excited states are sufficiently higher in energy, it is possible to neglect the coupling terms. However, there are numerous examples in the field of photo-chemistry or other ultra-fast processes in which the coupling cannot be neglected because the electronic energy levels are close together. Nevertheless, these non-Born Oppenheimer coupled systems can be successfully treated. Contrary to some statements made in the literature, it is not essential to apply the BOA in every case. More generally, the fact that the BOA does not violate the Heisenberg Uncertainty Principle and that it is possible to perform non-BOA calculations argues against the conclusion that chemistry cannot be reduced to quantum mechanics. Needless to say, it does not settle the more general question

of the reduction of chemistry but it does mean that other grounds would need to be invoked in order to sustain such a claim.

Acknowledgement

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Notes.

¹ I am grateful to Basile Curchod (University of Bristol) for drawing my attention to this aspect of the B-O approximation and for extensive discussion of BOA and the B-H representation.

² The remark was made to the author by Federica Agostini, a chemist specializing in the field on non-Born Oppenheimer chemical calculations.

³ This does not require the nuclei to be physically clamped however. The BOA only requires that kinetic energy tends to zero, not that it equals zero.

⁴ Once again, this stands as a flat contradiction of the quoted claims by some philosophers that chemists have no choice but to use the BOA and that there is no way to move beyond this approximation.

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