

ON THE QUANTUM THEORY OF MOLECULES:
RIGOUR, IDEALIZATION, AND UNCERTAINTY

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ABSTRACT. Philosophers have claimed that: (a) the Born-Oppenheimer approximation methods for solving molecular Schrödinger equations violate the Heisenberg uncertainty relations; therefore (b) so-called ‘quantum chemistry’ is not fully quantum; and so (c) chemistry does not reduce to physics. This paper analyses the reasoning behind Born-Oppenheimer methods and shows that they are internally consistent and fully quantum mechanical, contrary to (a)-(c). Our analysis addresses important issues of mathematical rigour, physical idealisation, reduction, and classicality in the quantum theory of molecules, and we propose an agenda for the philosophy of quantum chemistry more solidly grounded in scientific practice.

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1. INTRODUCTION

1.1. **Dethroning the Queen?** Quantum chemistry is the use of quantum mechanics (and quantum field theory) to model molecules and their dynamics, to explain and predict their chemical properties and reactions. Its status is important to questions about the place of physics among the sciences: prima facie, quantum chemistry is an example of the success of reductionism, exemplifying the fundamentality of physics with respect to chemistry and other natural sciences.¹ However, the received view in the philosophy of quantum chemistry is that attention to models and scientific practice reveals not only that quantum chemistry does not reduce to quantum physics, but that the two are explicitly in conflict. A principal argument for this view is based upon alleged *non-quantum* features of the ‘Born-Oppenheimer approximation’ (**BO**), which is the most commonly used model of molecular dynamics in quantum chemistry, and involves approximations including wavefunction separability, adiabaticity, and ‘clamping’. It has been claimed in the philosophy literature that **BO** violates the Heisenberg uncertainty principle, and so is in conflict with quantum theory.

¹There are of course different notions of both reduction and fundamentality, and at least both epistemic and ontic versions of each.

This claim has been developed in most detail by Olimpia Lombardi and coauthors (Lombardi and Castagnino 2010; González, Fortin, and Lombardi 2019; Fortin and Lombardi 2021; Lombardi 2023).² A further influential analysis is due to Chang (2015), who (citing a talk by Lombardi) asserts that:

...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 [...] 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 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, p. 198)

In our terms, Chang claims that **BO** involves both the separation of wavefunctions (which is what *he* calls ‘the Born-Oppenheimer approximation’) and a ‘clamping-down’ approximation, and that the latter violates the Heisenberg uncertainty principle, so the **BO** as a whole is not fully quantum. Lombardi (2023) puts the claim even more strongly. When endorsing Torretti’s (2000) view that bringing together theories without worrying about their incompatibility, seemingly ‘outrageously’ (p. 119), is nonetheless scientifically legitimate on pragmatic grounds, she notes:

The [Born-Oppenheimer], 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. (p. 115)

The Lombardi and Chang idea that **BO** *violates Heisenberg uncertainty* is the basis for more general anti-reductionist claims (Accorinti and González 2022; Cartwright 2022). Cartwright argues that this alleged conflict between the quantum chemistry of molecules

²See Woolley and Sutcliffe (1977); Woolley (1978); Claverie and Diner (1980) for the original quantum chemistry discussion. Hendry (Hendry (1998, 2006, 2010a,b, 2017); Accorinti and González (2022)) while taking an anti-reductionist stance, does not claim that **BO** violates the uncertainty relations. We do not address reduction in general, but our analysis is compatible with reduction, in the same spirit as Scerri (2012); Hettema (2017); Franklin and Seifert (2020); Seifert (2020, 2022); Scerri (2024b,a).

and Heisenberg uncertainty implies not only that chemistry fails to reduce to physics, but that the two are incompatible. This case is one of the main motivations for ‘dethroning the queen’ (i.e. not privileging physics among the sciences). After quoting the passage from Chang above (with no reference to Lombardi et al.), Cartwright says:

This approximation treats the atomic nucleus as a classical particle. 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. The approximations that provide the reduction violate the very theory that the chemistry is being reduced to [...] the success of quantum chemistry relies fundamentally on assumptions that belong to classical chemistry (Cartwright 2022, pp. 106-7)

To our knowledge, it has never been claimed in the scientific literature that **BO** violates the Heisenberg uncertainty principle.³ So either philosophers of science have uncovered an important scientific fact that scientists themselves have somehow missed, or the arguments of the philosophers are incorrect. One main aim of this paper is show the latter to be the case: ***BO** does not violate the Heisenberg uncertainty principle.*⁴ We show this by analysing a textbook-style presentation of **BO**. This analysis is of independent value since it identifies the idealizations that do and do not play a role in **BO**.

The second aim of this paper is to address concerns about the rigour of the textbook presentation of **BO**: in particular, subtle issues regarding the justification of the mathematical idealizations involved in modern formalisations. Sutcliffe and Woolley (2012) argue that assumptions regarding the discrete spectra of electronic Hamiltonians used in **BO** are unjustified. Furthermore, they suggest that removing these unjustified mathematical idealizations requires making use of resources of classical physics and empirical data introduced ‘by hand’. We consider the response to Sutcliffe and Woolley (2012) in Jecko (2014) and examine the latter’s argument that the mathematical idealizations can be justified without recourse to classical or empirical assumptions.

³This includes the notable discussions of Sutcliffe and Wooley cited earlier. The only scientific reference that we have found cited to support the violation claim is in Accorinti and González (2022). These authors quote remarks in (Villaveces C and Daza C 1990, pp. 100-1) that make reference to a potential contradiction between identifying a quantum chemical structure with a single point in a nuclear configuration space and the uncertainty principle as part of a motivation for moving beyond such an approach. No argument is provided that such a step is taken in context of **BO**.

⁴For related critical remarks see Scerri (2024b,a). We give a more thorough analysis, but the latter paper addresses related challenges beyond the scope of this paper.

The third and final aim of this paper is to use the analysis of **BO** to open up wider questions concerning the role of reduction and rigour in quantum chemistry. In §4 we provide a prospectus for future philosophical work on the foundations of quantum chemistry that is informed by scientific practice, as all parties agree that it should be. We argue that such philosophical work should be disentangled from the unwarranted mobilisation of quantum chemistry against the fundamentality of physics. We show that attending instead to the conceptual, formal and methodological questions which scientists themselves ask raises a range of issues and open questions relating to the various types of semi-classical modelling, the role of persistent environmental interactions, and the problem of isolating distinctively ‘chemical’ modes of quantum modelling practice.

1.2. The Idealization and Rigour Problems. When quantum chemists and physicists talk about **BO** they refer to an approach to solving the quantum mechanical equations for a molecule that builds on – but modifies and extends – pioneering work by Born and Oppenheimer in 1927. §2.1 provides a short history of the approach and its development, while §2.2 and §3 provide a detailed analysis of two levels of rigour of the modern form of the approximation. This section sets out schematic argument patterns for the analysis of the challenges to the modern **BO** in the sources cited above. First we sketch **BO** in simple terms. The basic idea is to use to the high ratio between the electron and nuclear masses to produce trial solutions to a molecular Schrödinger equation: we consider the time-independent equation, but the method extends to dynamical problems as well. There are two distinct aspects of **BO**: a *separation ansatz* and an *adiabatic approximation*. The ansatz is that the molecular wavefunction, $\Psi(x_1, x_2)$, is approximated by the product of a function of nuclei positions, $\theta_a(x_1)$, and a function of nuclei and electron positions, $\psi_a(x_1, x_2)$, so that we have: $\Psi(x_1, x_2) = \theta_a(x_1)\psi_a(x_1, x_2)$. The approximation is that the rate of change of the $\psi_a(x_1, x_2)$ with respect to the nuclear position is approximately zero; this condition provides an equation for $\theta_a(x_1)$.

The justification of **BO** is central to the idealization problem detailed below. The arguments of Lombardi and Castagnino (2010); González et al. (2019); Fortin and Lombardi (2021) (and perhaps also of Chang (2015), which endorses Lombardi’s analysis in the first quote above but does not otherwise elaborate) share a fundamental misrepresentation of how the approximation is justified in quantum chemical practice which is in terms of stability under de-idealization (as in many other cases). What then is the salient idealization of **BO**, and how is it justified? The intuitive idea is that the total

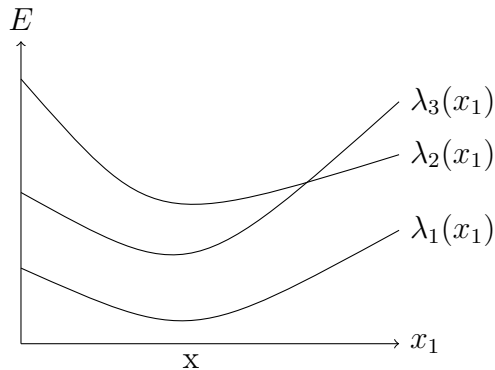


FIGURE 1. Eigenvalues λ_n of the clamped Hamiltonian, as (hypothetical) functions of the heavy, nuclear degrees of freedom x_1 . In the region around $x_1 = x$ the first three electronic energy levels can be seen to be widely separated: specifically, by far more than the kinetic energy of the nuclei. This is the condition for stable molecules, and for **BO**.

kinetic energy of the nuclei is small compared to the potential energy of the molecule and the total kinetic energy of the electrons. (This is because a nucleon is far heavier than an electron, and so typically moves far more slowly, and kinetic energy is mv^2). It is this energy difference that makes the molecular wavefunction $\Psi(x_1, x_2)$ effectively separable. *Mathematically*, $\psi_a(x_1, x_2)$ is an eigenstate of a so-called ‘clamped’ Hamiltonian: the sum of the potential energy of the molecule plus kinetic energy of the electrons only. It is best thought of as a *family* of electron (x_2) wavefunctions, one for each fixed nuclei configuration (x_1), with a corresponding *family* of energy eigenvalues $\lambda_a(x_1)$. Each family of eigenvalues then picks out a ‘potential energy surface’ as illustrated in Figure 1. (This part of **BO** is taken to somehow violate quantum theory, but it does not, as we explain in detail below.) $\theta_a(x_1)$ is, formally speaking, a wavefunction for the nuclei in this potential. The molecular energy is approximately the sum of $\lambda_a(x_1)$ with the nuclear kinetic energy, and because of the energy difference, close to the former. So if the gaps between the $\lambda_a(x_1)$ are large, only one $\psi_a(x_1, x_2)$ is relevant to $\Psi(x_1, x_2)$ – superposing with other eigenstates of the clamped Hamiltonian shifts the energy too far. Figure 1 shows the crucial representative features of the potential energy surfaces. It makes clear that energy gaps do not exist for all values of x_1 . It also illustrates that the gap can exist for a given range of values, about a minimum.

One expects that the nuclei of a stable molecule are restricted to a region around such a point; the nuclear wavefunction effectively vanishes outside. Thus the more specific assumption made in **BO** is:

Heavy: in a stable molecule the nuclei are approximately localized, in a quantum state in which their kinetic energy is much smaller than the electron kinetic energy (though not zero).⁵

The idealized model is one in which *Heavy* holds for *any* nuclear configuration, x_1 , corresponding to a stable molecule. That is, the energy gaps exist for *all* such values of x_1 , unlike the case shown in Figure 1. Inferences based upon such an idealized model are justified to the extent that they are stable under relaxing the idealization, and they remain approximately valid when x_1 is restricted to a given region. §2.2 considers the stability under de-idealization of the Born-Oppenheimer model found in a textbook presentation formalising the sketch just given. The approximate validity of the **BO** separation ansatz and the **BO** adiabatic approximation follows deductively from *Heavy* and this derivation is stable under de-idealization from an arbitrary to a specific range (see §2.2).⁶

The idealized model involves strictly false assumptions regarding the range of validity of *Heavy*, but does not involve any assertions inconsistent with quantum theory. By contrast, consider the following idealizing assumption:

Clamped: molecular nuclei have fixed definite positions and zero kinetic energy.

An idealized model of which *Clamped* is literally true would be one in which ‘clamped’ molecular nuclei have classical positions and momenta (namely zero), in conflict with the Heisenberg uncertainty principle.

In such a model it would be plausible to argue that a classical modelling procedure is required to apply the approximations involved. However, no evidence provided by the authors mentioned above that such an idealizing assumption is part of **BO** in either its original or modern form. Nor is the use of the *family* of clamped Hamiltonians equivalent to *Clamped*, which effectively selects one member of the family. As established in detail below, the modern form of **BO** makes explicit use of *Heavy* precisely as explained above.

⁵A more precise version – and rationale for the name – will be given in §2.2, once some of the necessary formalism has been set up.

⁶The adiabatic approximation can be expected to break down in various circumstances. The most obvious is when the nuclei are light, as with hydrogen. Yang et al. (2023) note: “considering the high mobility of light hydrogen atoms, the non-adiabatic coupling of different electronic states beyond the Born-Oppenheimer approximation is expected to be prominent” (p. 2). Such coupling gives rise to conical intersections between energy surfaces that are used to understand reaction pathways (Baer 2006). Much of current work in quantum chemistry goes beyond **BO** by considering the interactions between electronic and nuclear vibrational motion which leads to the coupling of different energy states of molecules (Yarkony 2012). See also Sibaev et al. (2020); Agostini and Curchod (2022)

This is a much logically weaker assumption than *Clamped* and consistent with the nucleus being a fully quantum particle.

Our argument regarding idealizations and **BO** is as follows:

The Idealization Problem

- I1. Idealized models are related to less idealized models via approximation relations.
- I2. Inferences based upon idealized models are justified if the features of the idealized model that ground the relevant inference are stable under de-idealization
- I3. The fundamental idealization of the BO model is *Heavy*. Inferences about the behaviour of molecules in the relevant regime are indeed stable under de-idealization
- I4. The BO model does not involve the idealization *Clamped*. Rather, a parameterised family of ‘clamped’ Hamiltonians are used as a tool to construct the effective molecular wavefunction in which the nucleus is fully quantum and the eigenstates of the full molecular Hamiltonian include an explicit nuclear kinetic energy term.
- I5. The conflict with the Heisenberg uncertainly relation (and stability under de-idealization) of *Clamped* is irrelevant to the use of models based on **BO**.

The second challenge to the **BO** concerns the *rigour* of certain assumptions about the spectrum of the clamped Hamiltonian in the separation ansatz. This *rigour problem* has not to our knowledge previously been discussed in the philosophy literature, but has been raised by important figures in quantum chemistry who have greatly influenced the philosophy of chemistry from a broadly anti-reductionist standpoint. Here we give a brief overview of the problem.

The derivation of the clamped Hamiltonian spectrum starts by expanding the molecular wavefunction: $\Psi(x_1, x_2) = \sum_a \theta_a(x_1) \psi_a(x_1, x_2)$. This expansion appears to be a mathematical fact, since (ignoring degeneracy) the ψ_a form a complete orthogonal basis because they are the eigenstates of a Hermitian operator. However, this reasoning assumes that the spectrum is discrete, when in fact it contains a continuous part, reached as the system ceases to be a stable molecule, and becomes an unbound collection of nuclei and electrons.⁷ One reasonable concern is that since in a continuous spectrum there are

⁷As explained below, discreteness of the bound state spectrum requires transforming to a centre of mass frame.

no normalizable eigenstates, **BO** does not, as it stands, lead to physical states. [Sutcliffe and Woolley \(2012\)](#) conclude from this that **BO** requires further classical assumptions that do amount to the introduction of fixed nuclear positions. They reason as follows:

It is thus not possible to reduce the molecular Schrödinger equation to a system of coupled differential equations of classical type for nuclei moving on potential energy surfaces [...] without a further approximation of an essentially empirical character. An *extra choice* of fixed nuclear positions must be made to give any discrete spectrum and normalizable [square-integrable] eigenfunctions. In our view this choice, that is, the introduction of the clamped-nuclei Hamiltonian, by hand, into the molecular theory is the essence of the “Born-Oppenheimer approximation” (p. 7)

Three related points: First, Sutcliffe and Wooley do not make explicit how ‘empirically fixing’ nuclei positions would solve the formal problems that they identify, so it is not clear exactly what they have in mind by this procedure; but at no point do they claim that **BO** violates Heisenberg uncertainty. Second, the problem that they raise is one of formal rigour, namely that **BO**, involves problematic mathematical simplifications, in particular assumption of normalizable eigenfunctions for operators without purely discrete spectra. One might thus plausibly understand this as a problem of justifying a ‘mathematical idealization’. Third, their conclusion that fixed nuclear positions must be put in ‘by hand’ only follows if that is the *only* way to deal with the rigour problem.⁸

Sutcliffe and Woolley’s reasoning perhaps suggests a version of *Clamped*, so could be taken as supporting the idealization argument in spirit (though not in technical detail). In any case, the rigour problem they raise is a valid challenge to textbook level presentations of **BO**. However, mathematical physicists have addressed it by reframing **BO** as approximating an eigenvalue and eigenstate of the total molecular Hamiltonian lying in the low energy, discrete part of its spectrum. §3 considers some of the details of this more rigorous treatment following the insightful work of [Jecko \(2014\)](#), which is both an overview of the mathematical literature on **BO**, and a response to various worries raised by [Sutcliffe and Woolley \(2012\)](#).

Our argument regarding rigour and **BO** is as follows:

⁸This paper is not focused on the work of Sutcliffe and Woolley, which is a critique of [Born and Huang \(1954\)](#), and does not fully detail their position. We do claim that justifying Born’s and Huang’s approach requires an assumption of (quantum) localization, which their text inadequately distinguishes from clamping.

The Rigour Problem

- (1) The textbook presentation of the BO model includes mathematical idealizations that presume the existence of normalizable eigenstates with discrete spectra.
- (2) A close analogue of *Clamped* is necessary to justify these mathematical idealizations, so the idealization problem putatively reoccurs in the context of trying to make the BO model rigorous (Sutcliffe and Woolley 2012).
- (3) However, the relevant mathematical idealization can be justified without appealing to anything like *Clamped*. (Jecko 2014).

2. THE BORN-OPPENHEIMER APPROXIMATION

2.1. The Historical Treatment. What we can call the ‘Perturbative Expansion Born-Oppenheimer approximation’ (**PBO**) is the approach to the approximate solution of the (time-independent) Schrödinger equation for stable molecules pioneered by Born and Oppenheimer in their 1927 paper *Zur Quantentheorie der Molekeln* (‘On the Quantum Theory of Molecules’).⁹ The key physical feature upon which the **PBO** is built is that nuclei are very much heavier than electrons. With this in mind Born and Oppenheimer introduce a small parameter, $\kappa = \left(\frac{m}{M}\right)^{\frac{1}{4}}$, where m is the electron mass and M the nucleon mass; the ratio m/M is roughly $1/2000$ so $\kappa \approx 0.15$. The crucial idea is to treat the nuclear kinetic energy as a perturbation of the energy, expanded in powers of κ . The original **PBO** is indicated by the authors to be valid from zeroth to fourth order in κ with nuclear vibrational energy corresponding to terms of second order and the rotational energy to fourth order in the energy. Coupling effects among electronic states appear beyond fourth order in κ .

The principal achievement of **PBO** is to show that one can use the electronic Hamiltonian for a fixed nuclear configuration to construct a family of electronic wavefunctions. These wavefunctions can then be used to calculate approximate eigenvalues for the full molecular Hamiltonian on the assumption that the nuclear motion is confined to a small vicinity of a privileged equilibrium configuration. Up to order κ^4 , approximate wavefunctions can then be written as products of ‘electronic’ wavefunction and ‘nuclear’ wavefunctions (Sutcliffe and Woolley 2012, p.3) (the physical significance of these objects is discussed in more detail in following sections).

⁹See Born and Oppenheimer (2000), Sutcliffe and Woolley (2012) and Scerri (2024b,a)

The seeds of later confusion were sown in the description that Born and Oppenheimer provide of the zeroth order equations. In particular, Part II of the paper, titled ‘Electronic Motion for Stationary Nuclei’ states that ‘if one sets $\kappa = 0$ one obtains a differential equation in the [electron position variables] alone, the [nuclear position variables] appearing as parameters’. The solution of such a ‘reduced’ equation is then indicated to ‘represent the electronic motion for stationary nuclei’. As noted by [Sutcliffe and Woolley \(2012\)](#), ‘it is perhaps to this statement that the idea of an electronic Hamiltonian with fixed nuclei as arising by letting the nuclear masses increase without limit, can be traced’. (p. 2).

Yet, the representational content of a perturbative model should not be conflated with its zeroth order terms, on pain of misunderstanding their ubiquitous use as scientific models. **PBO** does *not* represent the nuclei as fixed; rather it organizes an expansion in which the *only* leading, zeroth order, term has that character. That is, it expands around a *fictitious* system in which the nuclei are clamped. These are entirely different modelling strategies. (Analogously, one should not conflate a purely Newtonian model with a perturbative expansion involving the Newtonian model plus relativistic corrections.) The result of **PBO** is, of course, (in principle) a wavefunction that satisfies the uncertainty relations for both electrons and nuclei. Thus, the idealizing assumption *Clamped* does not form part of **PBO** and the idealization problem does not occur.

The **PBO** was made redundant by later work of [Born \(1951\)](#) and [Born and Huang \(1954\)](#), and it is that approach that is today referred to in chemistry literature as defining the “Born-Oppenheimer approximation” and to which we now turn.

2.2. A Textbook-style Presentation. This section is a treatment of the modern **BO**, drawing in parts upon [Messiah \(1962\)](#) and [Jecko \(2014\)](#) (but with no serious attempt at historical reconstruction). Here ‘textbook-style’ indicates both accessibility and an emphasis on heuristics over rigour at certain points. In particular, the pedagogical aim of a textbook may be to *sketch the overall logic* of a calculational method in order to emphasise certain principles, so that the method is memorable and portable to related problems in scientific practice. In the process, certain idealisations have to be made, which should be justified by a more rigorous de-idealisation in the background. Our treatment (which is similar to, but goes beyond standard presentations) similarly describes the overall logic of **BO** in a way to make clear its quantum nature; it makes certain idealisations, (some of) which are flagged below and addressed in detail in §3.

Suppose a system is comprised of two parts, with canonical variables $x_1 \in \mathbb{R}^m$ and $x_2 \in \mathbb{R}^n$. In the usual way, the state of the system in the x -representation – the wavefunction – is $\Psi(x_1, x_2) \in L^2(\mathbb{R}^m \times \mathbb{R}^n)$, and (setting $\hbar = 1$) the canonically conjugate observables are $i\partial/\partial x_j$. The (non-relativistic) Hamiltonian is the sum of kinetic, \hat{T}_j , and interaction, \hat{W} , parts:

$$(1) \quad \hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{W},$$

with \hat{W} some function of the variables x_j , and \hat{T}_j a power (or sum of powers) of the corresponding conjugate variables, $i\partial^n/\partial x_j^n$. In the case of a molecule, the first two terms will be the kinetic energies of nuclei and electrons ($\hat{p}_j^2/2m \propto -\partial^2/\partial x_j^2$), respectively, and the third, Coulombic potential energy.¹⁰

We are interested in finding the eigenstates of \hat{H} , which cannot be done analytically, but requires approximation. So suppose further – and this is the *crucial assumption* – that in the range of states of interest the kinetic energy of the x_1 subsystem is far smaller than both that of the x_2 part, and that of their interaction energy: $T_1 \ll T_2, W$ (where O denotes the expected value of observable \hat{O}). What ‘range of states’? In the first place, those wavefunctions that only have (non-negligible) support in a range of values of $\alpha < x_1 < \beta$; the first system is effectively localized within that region. (Moreover, the states should be below some maximum energy level.)

This condition (elaborated and sharpened below) is an *ansatz*, a temporary supposition made to find solutions, which must then be inspected to verify that they really solve the (time-independent) Schrödinger equation: if so the supposition is vindicated; if not then it must be given up. Of course, we seek motivation for making an *ansatz*, a reason to think that it will turn out to be vindicated. But such *motivation* should not be understood as its *justification* – if an *ansatz* is justified, it is wholly by its success in finding solutions. In the present case the *ansatz* is motivated by the composition of a molecule, in which the nuclei comprise the first system, and the electrons the second. In typical states, because electrons are 2000 times lighter than nucleons, they are more easily set in motion, and a stable state is one in which almost all the kinetic energy is in the motion of the former; if it is a low energy state then the nuclei can only be displaced from a potential energy minimum by a small amount (Messiah 1962, XVIII.12).

¹⁰One idealization has already been made; as discussed in §3, a total kinetic energy due to the velocity of the molecule as a whole should be subtracted.

Supposing the assumption holds, do the supposed solutions exist, justifying it? As a first step, consider normalized solutions to the (time-independent) Schrödinger equation for the so-called ‘clamped’ Hamiltonian:

$$(2) \quad (\hat{T}_2 + \hat{W}(x_1))\psi_a(x_1; x_2) = \lambda_a(x_1)\psi_a(x_1; x_2),$$

with $a = 1, 2, \dots$. Part of the spectrum of $\hat{T}_2 + \hat{W}(x_1)$ is continuous, so not all such states are normalizable, square-integrable functions. In this section we follow standard practice and ignore this complication. Here ‘clamped’ is understood purely formally – specific nuclear coordinates are picked out, but there is no implication that nuclei are physically located at x_1 . It is *as if* the light, electronic subsystem sees the heavy, nuclear subsystem at a fixed value of x_1 , so the Hamiltonian for that value is considered effective. Thought of this way, \hat{W} is a parameterized family of x_2 operators $\hat{W}(x_1)$: so there is not just one but infinitely many clamped Hamiltonians. In that case, the $\hat{T}_2 + \hat{W}(x_1)$ eigenvalues $\lambda_a(x_1)$ and eigenstates $\psi_a(x_1; x_2)$ are also parameterized families; hence the semi-colon. That is, formally speaking, the energy and state of the electronic subsystem vary for *fixed* energy level a , as x_1 varies. (Of course, whether or not the x_2 physically jump between energy levels – ‘potential energy surfaces’ – depends on the dynamics of the motion; we speak here only of the form of the spectrum.) From the *crucial assumption*, one next infers:

Heavy: the *gaps*, $|\lambda_n(x_1) - \lambda_m(x'_1)|$, between the $\lambda_a(x_1)$ s are much greater than the *values* of T_1 , when compared for any $\alpha < x_1, x'_1 < \beta$.

Clearly, this inference is not deductive; even if $T_1 \ll |\lambda_n(x_1) - \lambda_m(x_1)|$ for $\alpha < x_1 < \beta$, because $\lambda_n(x_1)$ varies with x_1 , it is possible that $\lambda_n(x_1) \approx \lambda_{n+1}(x'_1)$ for some values in that range. However, there should be sufficiently small ranges for which the condition holds, so what is really assumed is that there are eigenstates of \hat{H} whose support approximately lies in such a region. See Fig. 1. For a molecule, for instance, this amounts to the assumption that there are energy eigenstates in which the nuclei are sufficiently localized at the bottom of the potential energy well, which is quite reasonable for small excitation levels.

The reader may feel that a certain amount of hand waving is occurring; arguably it gets worse! However, our goal here is not to prove that **BO** is valid under certain conditions, but to give an intuitive account of the mathematical and physical significance of the conditions. The approximation has been subject to the more rigorous attentions

of mathematical physicists, so the argument outlined here rests on solid mathematical ground (see §3 and Jecko (2014)).

Before we show how **BO** uses *Heavy*, we should briefly say more regarding (2); since its meaning is at the heart of the interpretation of **BO**, this is not the final word. Because they are a set of eigenstates for a self-adjoint operator of the x_2 electron subsystem, for *each* nuclear $x_1 = X \in \mathbb{R}^m$ the $\psi_a(X; x_2)$ form a complete orthonormal basis: $\int \psi_a \psi_b dx_2|_{x_1=X} = \delta_{ab}$.¹¹ Thus (since in addition $\hat{T}_2 + \hat{W}$ commutes with x_1) any (x_1, x_2) wavefunction on $\mathbb{R}^m \times \mathbb{R}^n$ can be written:

$$(3) \quad \sum_a \theta_a(x_1) \psi_a(x_1, x_2).$$

Note that the RHS is *not* a sum of nuclear $\{\chi_a(x_1)\}$ and electron $\{\zeta_a(x_2)\}$ (tensor) product states:

$$(4) \quad \sum_a \chi_a(x_1) \zeta_a(x_2).$$

No, $\psi_a(x_1, x_2)$ represents a ‘direct integral’, taking, for each $x_1 \in \mathbb{R}^m$, an x_2 wavefunction $\psi_a(x_1; \cdot)$ satisfying (2) from a *distinct copy* of the $L^2(\mathbb{R}^n)$ Hilbert space. Both (3) and (4) give the general form of $L^2(\mathbb{R}^m \times \mathbb{R}^n)$ functions: the latter from the familiar properties of the tensor product; the former simply because specifying an $L^2(\mathbb{R}^n)$ function for each value of x_1 (in a suitably smooth way) specifies such a function – $\psi_a(X; x_2)$ is just the cross-section of $\psi_a(x_1, x_2)$ at $x_1 = X$.¹² So one cannot read (the terms in the sum) (3) as describing separate nuclear and electronic states: rather $\psi_a(x_1, x_2)$ is a wavefunction for *both* parts (unlike an electron wavefunction $\psi_a(X; \cdot)$). A lack of clarity regarding this situation, and perhaps specifically conflation of these two expansions, has contributed to confusion regarding the interpretation of **BO**, discussed in §2.3.

Proceeding with our explication of the approximation itself, *Heavy* has two important (though equivalent) consequences whose derivation we now sketch.¹³ The arguments are

¹¹Here we make the important idealisation that the spectrum is discrete, which applies at many points in the following.

¹²Thus contrast (3), with (2); the former expresses a function over $\mathbb{R}^m \times \mathbb{R}^n$, while the latter expresses a continuous infinity of equations for x_2 wavefunctions, one for each value of x_1 . The use, in ψ_a , of a comma in former versus a semi-colon in the latter indicates just this difference.

¹³The following arguments are presented without careful attention to the distinction between x_1 -parameterized families of wavefunctions and operators on the one hand, and their direct integrals on the other. They are best read as equations relating the corresponding differential operators and functions in the position representation, which is indifferent to the distinction.

straightforward, and in both cases the important point is that they follow from *Heavy* alone (with no appeal to *Clamped*).

Derivation 1. Separability Ansatz from Heavy. There are eigenstates of \hat{H} with the approximate form $\theta_a(x_1)\psi_a(x_1, x_2)$: the so-called ‘Born-Oppenheimer ansatz’. To see this, suppose (for reductio) that the E -valued energy eigenstate $\Psi(x_1, x_2)$ has non-negligible contributions from two¹⁴ different (orthonormal) $\theta_a(x_1)\psi_a(x_1, x_2)$, with energies $\lambda_m(x_1) < \lambda_n(x_1)$:

$$\begin{aligned}
 \hat{H}\Psi &= \hat{H} \frac{1}{\sqrt{2}}(\theta_m\psi_m + \theta_n\psi_n) = \frac{E}{\sqrt{2}}(\theta_m\psi_m + \theta_n\psi_n) \\
 (5) \quad &= (\hat{T}_1 + \hat{T}_2 + \hat{W}) \frac{1}{\sqrt{2}}(\theta_m\psi_m + \theta_n\psi_n) \\
 &= \hat{T}_1 \frac{1}{\sqrt{2}}(\theta_m\psi_m + \theta_n\psi_n) + \frac{\lambda_m}{\sqrt{2}}\theta_m\psi_m + \frac{\lambda_n}{\sqrt{2}}\theta_n\psi_n,
 \end{aligned}$$

using (1) and (2). (In the final step we use the fact that \hat{T}_2 contains only x_2 derivatives, while \hat{W} is a function of x_1 and x_2 , so both operators commute with $\theta_a(x_1)$). The following argument does not depend on our simplifying assumption of equal, real amplitudes.

The sum of the second two terms is a vector that fails to be parallel to Ψ by a vector whose amplitude is the order of $(\lambda_n - \lambda_m)/\sqrt{2}$: for instance, one could either add $(\lambda_n - \lambda_m)\theta_m\psi_m/\sqrt{2}$ or subtract $(\lambda_n - \lambda_m)\theta_n\psi_n/\sqrt{2}$. That is to say, by (5) – namely the supposition that Ψ is an eigenstate – we have

$$(6) \quad \left| \hat{T}_1 \frac{1}{\sqrt{2}}(\theta_m\psi_m + \theta_n\psi_n) \right| \approx (\lambda_n - \lambda_m)/\sqrt{2}.$$

But for any Hermitian operator and normalized vector, $|\hat{O}\phi|$ cannot exceed the greatest eigenvalue. So in this case, by *Heavy*,

$$(7) \quad \left| \hat{T}_1 \frac{1}{\sqrt{2}}(\theta_m\psi_m + \theta_n\psi_n) \right| \leq T_1^{max} \ll (\lambda_n - \lambda_m)/\sqrt{2},$$

a manifest contradiction. Hence the supposition is false, and an eigenstate of total energy cannot be a sum of $\theta_a\psi_a$, but has the product form

$$(8) \quad \hat{H}\Psi_a(x_1, x_2) \approx \hat{H}\theta_a(x_1)\psi_a(x_1, x_2) \approx E_a\theta_a(x_1)\psi_a(x_1, x_2).$$

□

¹⁴This assumption is not innocuous as strictly the following depends on it; it is however illustrative of the role energy gaps play in **BO** in general.

Put another way, such states (approximately) *diagonalize* the total Hamiltonian: there are no cross-terms for such states with different values of a .

Derivation 2. Adiabatic Approximation from Heavy. Recall that the position representation of \hat{T}_1 has the form $\partial^2/\partial x_1^2$:

$$(9) \quad \hat{T}_1 \theta_a \psi_a \propto \frac{\partial^2}{\partial x_1^2} \theta_a \psi_a = \frac{\partial^2 \theta_a}{\partial x_1^2} \cdot \psi_a + 2 \frac{\partial \theta_a}{\partial x_1} \cdot \frac{\partial \psi_a}{\partial x_1} + \theta_a \cdot \frac{\partial^2 \psi_a}{\partial x_1^2}.$$

However, $\theta_a \psi_a$ diagonalizes both $\hat{T}_2 + \hat{W}$ using (2), and (approximately) $\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{W}$ from (8). Therefore it also (approximately) diagonalizes \hat{T}_1 : $\langle \theta_b \psi_b | \hat{T}_1 | \theta_a \psi_a \rangle \propto \delta_{a,b}$. In the x_1 -representation,

$$(10) \quad \int dx_1 \theta_b^*(x_1) \int dx_2 \psi_b^*(x_1, x_2) \left\{ \frac{\partial^2 \theta_a}{\partial x_1^2} \psi_a + 2 \frac{\partial \theta_a}{\partial x_1} \frac{\partial \psi_a}{\partial x_1} + \theta_a \frac{\partial^2 \psi_a}{\partial x_1^2} \right\} \propto \delta_{a,b}.$$

Since different ψ_a are orthogonal (since distinct eigenstates) the x_2 integral means that the first term in the sum is proportional to $\delta_{a,b}$. However, neither of the derivatives of ψ_a will be orthogonal to ψ_b (and similarly for the θ s), so that the remaining terms will not be proportional to $\delta_{a,b}$ – unless they are both zero. Thus (10) entails that

$$(11) \quad \frac{\partial \psi_a(x_1, x_2)}{\partial x_1} \approx 0,$$

(which is the more specific statement that often goes under the name the ‘Born-Oppenheimer approximation’).

□

Note that (11) is ‘adiabatic’ in the sense that ψ changes ‘slowly’ with respect to x_1 , not time (c.f. [Huggett and Thébault \(2023\)](#)).

Making the adiabatic approximation (11) in (9) yields

$$(12) \quad \hat{T}_1 \theta_a \psi_a = \psi_a \frac{\partial^2 \theta_a}{\partial x_1^2} = \psi_a \hat{T}_1 \theta_a.$$

Hence, the significance of the ansatz and approximation is that the part of the joint state $\Psi_a(x_1, x_2)$ that expresses the kinetic energy of the nuclei can (approximately) be factored out as $\theta_a(x_1)$. But to repeat the discussion after (3), it cannot be over-emphasized that $\Psi_a(x_1, x_2)$ has *not* been factored into strictly nuclear and electronic parts, since the other factor, $\psi_a(x_1, x_2)$, depends on both, not just the electron configuration.

We are now in a position to solve the molecular energy eigenstate problem for the system. From (8), one needs to find $\theta_a(x_1)$ and $\psi_a(x_1, x_2)$; the latter is given by (2), so

all we need is the equation for the former. From (8) we have:

$$(13) \quad (\hat{T}_1 + \hat{T}_2 + \hat{W})\theta_a(x_1)\psi_a(x_1, x_2) \approx E_a\theta_a(x_1)\psi_a(x_1, x_2),$$

while from (2) and (12) we have

$$(14) \quad \approx (\hat{T}_1\theta_a(x_1)) \cdot \psi_a(x_1, x_2) + \lambda_a(x_1)\theta_a(x_1)\psi_a(x_1, x_2),$$

which gives:

$$(15) \quad (\hat{T}_1 + \lambda_a(x_1) - E_a)\theta_a(x_1) \approx 0.$$

This has the *form* of a (time-independent) Schrödinger equation for the nuclear variables, ‘living’ on a potential energy surface $\lambda_a(x_1)$, but recall the discussion after (12). That cannot be the correct *literal* description of the nuclei in **BO**, since *both* $\theta_a(x_1)$ and $\psi_a(x_1, x_2)$ represent aspects of the nuclear subsystem.

To sum up, from the Born-Oppenheimer separation ansatz (8), finding the approximate eigenstates $\Psi(x_1, x_2)$ of \hat{H} reduces to finding solutions to (2) and (15), and taking their product, a significant simplification. (Of course, these equations can still not be solved analytically, and require further approximations, for instance the WKB approximation.) *Together* these steps constitute **BO**.

2.3. Idealization and Uncertainty. At the heart of the interpretation of **BO** is the use of (2), in which the nuclei might *appear* to be represented as being ‘clamped’ in place. If this were literally the case, then they would be regarded as classical at this stage of the method. But recall our discussion of (3): the resulting electron wavefunctions are found simply in order to formally express the full molecular wavefunction $\Psi(x_1, x_2)$ in a useful way.

As pointed out above, the subsystem wavefunction for a given parameter value, $\Psi(X; \cdot)$, is the cross-section of the full wavefunction, $\Psi(x_1, x_2)$ at $x_1 = X$, with no physical significance of its own. (One might say that it is the probability amplitude for the x_2 subsystem conditional on the x_1 subsystem ‘being found at’ x_1 , but that would be taken with the usual grain of salt when we speak of quantum quantities with continuous spectra taking on a definite value.) Conversely, $\Psi(x_1, x_2)$ is the direct integral of a parameterized family of eigenfunctions, $\Psi(x_1; \cdot)$. Moreover, given a family of bases $\psi_a(x_1; \cdot)$ for $L^2(\mathbb{R}^n)$, and their direct integral $\psi_a(x_1, x_2)$ it is a mathematical fact that the total wavefunction $\Psi(x_1, x_2)$ can be expanded as $\sum_a \theta_a(x_1)\psi_a(x_1, x_2)$ for some functions $\theta_a(x_1)$.

In **BO** one solves (2) for every value of x_1 , and since each clamped Hamiltonian is Hermitian, there is a family of bases, which one uses to expand $\Psi(x_1, x_2)$, the wavefunction of the full system, both electrons and nuclei. Note that this procedure involves no approximations at all (given the mathematical idealization of a discrete spectrum, to be discussed in §3); approximations are used later to select just one term in the sum, and to find an equation for the $\theta(x_1)$. In short, the use of the clamped Hamiltonian (or rather, infinity of clamped Hamiltonians) is purely formal, for constructing a useful expansion, and should not be given physical significance. *At no stage in the method does **BO** represent the nuclei to be anything but quantum.*

One might contrast this direct integral with a tensor product expansion, which, while also being formal, ascribes wavefunctions to subsystems that we take to represent the physical states of them in the joint system. In the direct integral formalism, the subsystem wavefunction $\psi_a(X, x_2)$ does not provide such a representation; at best it represents the physical state an electron *would* have if it were in Coulomb potentials centred at the X , and not *actually* interacting with quantum nuclei. But even this interpretation is irrelevant to the fact that **BO** utilizes a formal decomposition of the quantum state of the molecule; there simply is no requirement that its elements have a physical interpretation at all. (And of course we should continue to distinguish **BO** from the very simple approximation in which the nuclei are treated as classical charges at the minimum, x , of the potential energy surface, in which idealization there is no molecular wavefunction at all, just an electron wavefunction.)

All the states relevant to **BO** are vectors in a Hilbert space in which the Heisenberg uncertainty relations are automatically respected. This is because wavefunctions are square-integrable functions on (configuration) space $L^2(\mathbb{R}^k)$. For instance, for a single degree of freedom the variances of position and momentum variables are: $\sigma_x^2 = \int_{-\infty}^{\infty} x^2 \cdot |\psi(x)|^2 dx$ and $\sigma_p^2 = \int_{-\infty}^{\infty} p^2 \cdot |\tilde{\psi}(p)|^2 dp$, where $\psi(x)$ and $\tilde{\psi}(p)$ are the position and momentum basis wavefunctions, respectively. The Heisenberg uncertainty relation, $\sigma_x \sigma_p \geq \frac{\hbar}{2}$, is a simple mathematical consequence of the fact that position and momentum are Fourier conjugates.

A violation of the relation would require a ‘wavefunction’ sharply peaked in *both* the position and momentum basis simultaneously, contrary to this basic fact about QM and **BO**. They would only be violated if, the model represented electron or nuclei states as other than vectors in Hilbert space: say, as a delta functions in both position and

momentum space.¹⁵ Similarly, that the ‘nuclear wavefunction’ $\theta_a(x_1) \in L^2(\mathbb{R}^m)$ is a vector in a Hilbert space means that it cannot violate the Heisenberg uncertainty relation; it does not and cannot violate the Heisenberg uncertainty relation. (The scare quotes remind the reader that the ‘electronic wavefunction’ $\psi_a(x_1, x_2)$ also plays a role in representing the state of the nuclei.)

Moreover, as already noted, it would be a mistake to naïvely interpret $\Psi_a(x_1, x_2)$ as being factored into strictly nuclear and electronic parts. The factor, $\psi_a(x_1, x_2)$, depends on the nuclear configuration, not just the electron configuration. The role of ‘classical’ parameters and the ‘clamped’ Hamiltonian in constructing $\psi_a(x_1, x_2)$ is entirely irrelevant to the status of the nuclei as quantum particles. **BO** provides an *inherently quantum* representation of molecular structure that does not admit a classical separation into purely electronic and nuclear representations. The quantum nature of the nuclei in **BO** is highlighted in the discussion of Jecko (2014) who notes in his concluding section: ‘We emphasise that, in the mathematical treatment of the Born-Oppenheimer approximation, the nuclei are always considered as quantum particles. The use of clamped nuclei is just a tool to construct an appropriate effective Hamiltonian but the latter is a quantum, nuclear Hamiltonian with restricted electronic degrees of freedom’ (Jecko 2014, p. 20).

3. ON THE MATHEMATICAL TREATMENT OF BORN-OPPENHEIMER

We now turn to the question of rigour in textbook treatments of **BO** and consider features of the modern mathematical **BO** approximation that are sufficient to allay the relevant concerns. Recall that Sutcliffe and Woolley (2012) claim that the clamped Hamiltonian in general has a continuous part to its spectrum; physically plausible, for energies at which the constituents have disassociated, and there is not longer a stable molecule. Thus some further ingredient is needed to underwrite modelling a molecule with normalizable square-integrable eigenfunctions with a discrete spectrum. They suggest that extra empirical input and classical assumptions are required to deal with this issue. This is the ‘rigour problem’ introduced above, to which we now return. We follow Jecko (2014), which identifies three principal problems with textbook treatments of **BO**.¹⁶

¹⁵See Footnote 24 for a short discussion of precisely such a possibility in the context of mixed classical-quantum models in which there is failure of positivity of the density matrix in the quantum part of the model. As discussed there, this is understood by the scientists themselves as a pathological feature of the models rather than a putative representation of Heisenberg uncertainty violation.

¹⁶Thierry Jecko has also emphasized to us in correspondence that there are rigorous approaches to the quantum treatment distinct from **BO**, for instance the ‘exact factorization’ of Abedi et al. (2010).

First, the analysis only involves the internal energy of the molecule, even though it has centre of mass motion and associated kinetic energy, with a continuous spectrum (absent boundary conditions). To separate out the internal levels (to find the spectrum, or the spatial structure, or for scattering) one can transform to a centre of mass frame (of the molecule or just its nuclei, depending on the problem), and subtract the centre of mass kinetic energy. This procedure introduces a new term into the Hamiltonian (the Hughes-Eckart energy), which is suppressed by the ratio of electronic to nuclear masses ($\sim 10^{-3}$), so is neglected in low order approximation.¹⁷ This complication is harmless for present purposes, so we suppressed it for reasons of space.

The second problem arises because the expansion (3) is not really a sum, but a sum of low energy states plus an *integral* over states in the high energy, continuous part of the spectrum of $\hat{T}_2 + \hat{W}$. As is familiar, in any continuous spectrum there are no normalizable eigenstates, something finessed in familiar ways by physicists via the Dirac delta function, and more rigorously by the theory of ‘spectral decomposition’. However, in the present case details of the structure of the spectrum, in particular the existence of ‘thresholds’, (Jecko 2014, §V), make the expansion highly non-trivial, and hard to control. Its existence is thus – from a mathematically rigorous point of view – an ‘in principle’ matter only.

The third problem is that the appropriate formalism for a mathematically rigorous treatment is, as mentioned earlier, that of the *direct integral* (Reed and Simon 1978, 280-7). Any $L^2(\mathbb{R}^m \times \mathbb{R}^n)$ function $f(x_1, x_2)$ is understood as an $L^2(\mathbb{R}^n)$ -valued function $f(x_1, \cdot)$ with $x_1 \in \mathbb{R}^m$. One then naturally defines the direct integral of a parameterized family of operators $\hat{O}(x_1)$ on $L^2(\mathbb{R}^n)$, as the operator \hat{O} on $L^2(\mathbb{R}^m \times \mathbb{R}^n)$ whose effect on $f(x_1, x_2)$ is the direct integral of $\hat{O}(x_1)f(x_1, \cdot)$: i.e., it acts on each x_2 function as the appropriate operator in its state space.¹⁸

In response to the last two problems, mathematical physicists have a somewhat different perspective on **BO** to that of §2.2. The goal is to approximate an eigenstate (and eigenvalue) lying in the low energy, discrete part of the spectrum of the molecule (1). To do this, one considers eigenstates of the Hamiltonian *projected* onto the subspace in which its spectrum is discrete. See (Jecko 2014, §IV) for details of the following sketch. Let us call $\hat{T}_2 + \hat{W}$, the direct integral of the clamped Hamiltonians $\hat{T}_2 + \hat{W}(x_1)$, the ‘reduced Hamiltonian’. While the latter acts on $L^2(\mathbb{R}^n)$, the state space of the electron

¹⁷Sutcliffe and Woolley (2012) caution that ignoring it can make the Hamiltonian ill-defined.

¹⁸There are important questions of the self-adjointness of the various Hamiltonians involved. And we continue to ignore degeneracy in the spectrum.

subsystem, the former acts on $L^2(\mathbb{R}^m \times \mathbb{R}^n)$, the state space of the full system, including both the electrons *and the nuclei*: both, that is, are treated quantum mechanically. It is also called the ‘electronic Hamiltonian’, but that would be misleading for our purposes since it acts on the state of the whole molecule. Analogously for the projection operator: for a given $x_1 = X$ and a *finite discrete* range of eigenstates $\psi_a(X; x_2)$ of $\hat{T}_2 + \hat{W}(x_1)$ there is an operator

$$(16) \quad \hat{P}(X)f(x_2) = \sum_{a=1}^N \psi_a(X; x_2) \int \psi_a^*(X; x_2) f(x_2) dx_2$$

projecting $f(x_2) \in L^2(\mathbb{R}^n)$ onto the subspace spanned by the $\psi_a(X; x_2)$. \hat{P} , the direct integral of the $\hat{P}(x_1)$, then projects states in $L^2(\mathbb{R}^m \times \mathbb{R}^n)$ onto the discrete subspace spanned by the corresponding $\psi_a(x_1, x_2)$ eigenstates of the electronic Hamiltonian. Since \hat{P} also acts on the full molecular states space, it too treats nuclei as well as electrons as quantum mechanical.

To overcome the issue of a continuous spectrum, the first approximation made is to seek eigenstates of the *projected* molecular Hamiltonian $\hat{H}_{\text{eff}} = \hat{P}(\hat{T}_1 + \hat{T}_2 + \hat{W})\hat{P}$, instead of $\hat{T}_1 + \hat{T}_2 + \hat{W}$. One assumes that if an eigenstate of the latter exists in a given narrow range of the energy, then it can be approximated by an eigenstate of the former lying in the same range: *one replaces the tricky problem of solving the ‘true’ Hamiltonian with the simpler problem of solving an effective Hamiltonian for the energy range of a stable molecule*. Formally, \hat{H}_{eff} acts on $L^2(\mathbb{R}^m \times \mathbb{R}^n)$: first a state is projected onto the $\psi_a(x_1, x_2)$ subspace, then acted on by the molecular Hamiltonian, and the result projected again onto the subspace. \hat{H}_{eff} too treats both nuclei and electrons as quantum. Note that the effect of \hat{H}_{eff} is always to produce a vector in, V , the *finite* dimensional subspace spanned by the $\psi_a(x_1, x_2)$, so (a) all states orthogonal to V are eigenstates of \hat{H}_{eff} with eigenvalue 0, and (b) all its other eigenstates lie in V , and so have finite cardinality. In relation to §2.2, one has made rigorous (3), now understood as expanding solutions of the Schrödinger equation for the *projected* Hamiltonian.

Sutcliffe and Woolley (2012) argue that the direct integral decomposition of the unprojected reduced Hamiltonian entails that it has a purely continuous spectrum, and hence that the expansion assumed at the start of BO is invalid (p. 6). Their argument is not entirely explicit, but plausibly they are appealing to Theorem XIII.86 of Reed and Simon (1978) (work which they cite elsewhere). However, such an appeal is inapplicable to the *projected* reduced Hamiltonian, since one of the conditions of the theorem is an

infinite spectrum, which is exactly what the projection destroys. They are correct that empirical input, namely the relevant range of energies, is used in the rigorous **BO**, but that does not make the model not quantum. (Nor does it seem a failure of reduction that a derivation not be carried out entirely from first principles; the approximation itself is justified rigorously, and the empirical input merely tells us that the system is in the range in which it holds. Moreover the use of the approximation can be vindicated post hoc by showing that the relevant conditions hold.)

The previous section shows that textbook **BO** is fully quantum, and adding a step in which the reduced Hamiltonian is projected onto a discrete part of its spectrum in no way undermines that argument. The projected Hamiltonian is still quantum, indeed a quantum theoretical approximation to the quantum reduced Hamiltonian. The difference is rather that **BO** is no longer understood as the lowest order in some well-defined exact expansion, but rather as an approximation, with some well-understood corrections, to an exact solution. This situation is in contrast, not only to our textbook style presentation, but also to those of Born and Oppenheimer, Born and Huang, and Messiah; while more careful than ours, theirs remain heuristic.¹⁹ Once the appropriate formal machinery has been deployed, **BO** can be formalised to the standards of rigour of mathematical physics. Moreover, the arguments of [Sutcliffe and Woolley \(2012\)](#) can be evaded in a rigorous *quantum* treatment, and they do not indict the mere appearance of the clamped Hamiltonian in **BO**. Hence, the anti-reductionist arguments in philosophy of chemistry are not only unwarranted and incorrect, but also misidentify the salient challenge to the status of the **BO**.

4. RIGOUR AND REDUCTION IN QUANTUM CHEMISTRY

This final section considers questions of mathematical rigour and reduction in quantum chemistry more generally. Many of the questions raised in this section track elements of the Sutcliffe and Woolley exchange with Jecko.

Let us start with the role of ‘classical’ assumptions in the emergence of ‘determinate molecular structure’. Let us first assume that what is meant by ‘determinate molecular structure’ is provided by the regime in which the adiabatic approximation is valid, and thus the nuclei are such that the variation of the ‘electron’ wavefunction with respect to nuclear positions is approximately zero. §2-3 show exhaustively that the emergence of such structure requires neither classical assumptions in the sense of clamped nuclei, nor

¹⁹See ([Jecko 2014](#), §V) for a detailed comparison.

violation of the uncertainty relation. Rather the assumption required for **BO** is *Heavy*, which is entirely consistent with a fully quantum treatment of the molecule. There is a richer notion of molecular structure that includes the number, angles and lengths of chemical bonds and chirality (Franklin and Seifert 2020). **BO** is far from sufficient to model such structure, although plausibly in some circumstances it may prove necessary.²⁰ In this context, there is debate about the requirement for a solution to the measurement problem of quantum theory in order to account for the emergence of molecular structure (Franklin and Seifert 2020; Fortin and Lombardi 2021; Seifert 2022; Miller 2023). It remains to be seen whether there are any fundamental differences between foundational problems in quantum chemistry and other applications of quantum mechanics to matter systems.

More generally, in the context of discussions of ‘classical’ and ‘semi-classical’ assumptions our positive proposal is as follows. Firstly, models such as **BO** should be described as ‘quantum’ models of molecules, since all aspects of the molecules are treated quantum mechanically.

Secondly, one may legitimately deploy the term ‘semi-classical’ in a broad sense to indicate an application of quantum theory in which, while the system is treated quantum mechanically, the model includes radiative fields that are not. In this sense, the original quantum theory of the atom, as well as the modern quantum-mechanical treatment, is ‘semi-classical’ since the electromagnetic field through which the nucleus and the electrons interact is not quantized, cf. (Boucher and Traschen 1988). Similarly for most of quantum chemistry including **BO**. It would be moot to claim that chemistry does not reduce to quantum physics because the physics in question is semi-classical in this sense, because huge amounts of what is ordinarily called ‘quantum physics’ is! (E.g., standard non-relativistic quantum-mechanics other than free particles, including most condensed matter physics.) Such semi-classical physics is a kind of quantum physics.

Thirdly, one should distinguish various more specific meanings of ‘semi-classical’. One refers to a quantum mechanical expansion, in terms of classical zeroth order plus quantum corrections, which is truncated at some order in \hbar (or other parameter such as mass ratios) to provide an approximate model.²¹ In such cases, the semi-classical model

²⁰It is certainly not the case that the **BO** is necessary in general. See Footnote 6 for references on quantum chemistry *beyond* the **BO**.

²¹The two most important examples are when such a truncation is made in a quantum moment expansion (typically leading to Ehrenfest type equations) or in an expansion for the wavefunction (typically leading to a WKB-approximation).

is a sub-model within the general framework of quantum theory.²² A formally closely related, but physically and conceptually different, sense of ‘semi-classical’ is found in the context of certain ‘semi-classical’ approaches to gravity where the field equations are rewritten in terms of classical metric variables on the left-hand side but the first moment (i.e. expectation value) of the stress-energy tensor is inserted on the right-hand side. A further notion of semi-classicality refers to specific behaviour in the limit (usually $\hbar \rightarrow 0$) in which the classical theory obtains.²³ Finally, the term ‘semi-classical’ is applied to mixed classical-quantum models which simultaneously feature representations of classical and quantum states and dynamics. The former in terms of classical phase space states and Poisson bracket structure and the latter in terms of operators, density matrices and commutator brackets structure.²⁴

It is useful to distinguish the distinct modelling contexts in which semi-classical models, in one or more of the more specific senses, might be deployed within quantum chemistry and articulate the relevance for reductive explanations in each context. They are as follows. (1) *Mathematical Idealization*: The model is being used to represent a fully quantum phenomena and the semi-classical features are a mathematical idealization that relates the semi-classical effective model to a (less) idealized fully quantum model. Given the stability of salient explanatory features under de-idealization there no potential problem for reductive explanations of the relevant phenomena. (2) *Physical Idealization*: The model is being used to represent a fully quantum phenomena but this representation is via proxy model of semi-classical phenomena that approximate the quantum phenomena for the purposes and degree of accuracy required. Again, there is no problem for reductive explanations given stability of the salient explanatory features under de-idealization (Bokulich 2008, 2017). (3) *Emergent Phenomena*: The model is being used to represent

²²We thus recover the idea familiar from Nickles reduction of a successor theory containing a version of the predecessor theory via the application of a set of mathematical operations to its models (Palacios 2022).

²³Such cases have been much discussed in the physics and philosophy of physics literature (Berry 1977, 2001; Batterman 2001; Bokulich 2008; Rosaler 2015; Steeger and Feintzeig 2021) and they merit study in the context of quantum chemistry.

²⁴Mixed classical-quantum models have been widely applied in non-adiabatic quantum chemical modelling (Tully 1991; Crespo-Otero and Barbatti 2018) and bring up various interesting issues that are worthy of philosophical engagement. For example, in this context there is the possibility of failure of positivity of the density matrix in the quantum part of the model which, in turn, allows the possibility of inconsistency with the Cauchy-Schwartz inequality that would be required for the violation of Heisenberg uncertainty type relations (Bondarenko and Tempelaar 2023; Gay-Balmaz and Tronci 2023). Significantly, such a feature is understood by the scientists themselves as a pathological feature of the models rather than a putative representation of Heisenberg uncertainty violation or, moreover, a failure of reduction. Indeed, work on the topic takes density matrix positivity to be a precondition of physically consistent mixed classical-quantum dynamics.

emergent semi-classical phenomena that occur in the context of classical-quantum limit behaviour. There is a putative problem for any account of reductive explanation that is incompatible with emergence qua novel and robust behaviour, but not for any account of reductive explanation that is so compatible, cf. (Bokulich 2008; Butterfield 2011; Franklin 2024).

A further issue is the role of the environment (Ladyman and Thébault 2024). In this context, Sutcliffe and Woolley (2012) say ‘one should not expect useful contact between the quantum theory of an isolated molecule and a quantum account of individual molecules, as met in ordinary chemical situations where persistent interactions (due to the quantized electromagnetic field, other molecules in bulk media) and finite temperatures are the norm.’ (p. 7). These remarks, together with related ideas developed by Seifert (2022), form a fruitful basis for an ‘open systems view’ of quantum chemistry in the manner recently proposed for quantum physics more generally by Cuffaro and Hartmann (2021). We expect that such a view would prove to be consistent with any suitably nuanced understanding of model-based understanding of reduction and idealization.²⁵

We conclude with the following questions: Is there a methodological distinction between the use of models in modern quantum chemistry, and other examples of quantum modelling practice in matter systems, such as applications of quantum mechanics to solid state or few body systems? Is there space for distinctively ‘chemical’ modes of quantum modelling practice? In answering such questions philosophers need to re-conceptualise the physics-chemistry interface with quantum chemistry recast as a ‘littoral zone’, with its own distinctive modelling ecology, influenced by both disciplines. The distinctive chemical features in the methodology of quantum chemistry are rooted in experimental practices, such as spectroscopy, rather than formal features of the models.

²⁵Whilst it is common in quantum chemistry to model molecules as if they were isolated from their environment, real molecules interact with other systems as per the quote from Sutcliffe and Woolley (2012). However, in models of an ‘isolated’ quantum system the effects of the environment may be added in to produce an ‘autonomous’ open system model, just as the effect of friction can be represented via an autonomous model of an ‘isolated’ oscillator Ladyman and Thébault (2024). We may thus, following Seifert (2022), understand the use of non-Coulombic Hamiltonians in quantum chemistry as a means of encoding persistent environmental interactions in a manner analogous to the use of non-conservative forces in other physical modelling contexts. The structure of such ‘open quantum chemistry’ models is closely related to physical models of environmental decoherence. The connection between emergence-reduction in the context of decoherence (Wallace 2012; Joos et al. 2013; Dawid and Thébault 2015; Franklin 2024) and ‘open quantum chemistry’ deserves further study.

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REFERENCES

- Abedi, A., N. T. Maitra, and E. K. U. Gross (2010, Sep). Exact factorization of the time-dependent electron-nuclear wave function. *Phys. Rev. Lett.* 105, 123002.
- Accorinti, H. L. and J. C. M. González (2022). Models and idealizations in quantum chemistry: The case of the born-oppenheimer approximation. *Philosophical Perspectives in Quantum Chemistry*, 107–124.
- Agostini, F. and B. F. Curchod (2022). Chemistry without the born-oppenheimer approximation.
- Baer, M. (2006). *Beyond Born-Oppenheimer: electronic nonadiabatic coupling terms and conical intersections*. John Wiley & Sons.
- Batterman, R. W. (2001). *The devil in the details: Asymptotic reasoning in explanation, reduction, and emergence*. Oxford University Press.
- Berry, M. V. (1977). Semi-classical mechanics in phase space: a study of wigner’s function. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences* 287(1343), 237–271.
- Berry, M. V. (2001). Chaos and the semiclassical limit of quantum mechanics (is the moon there when somebody looks?). *Quantum Mechanics: Scientific perspectives on divine action* 41, 56.
- Bokulich, A. (2008). Reexamining the quantum-classical relation. *Reexamining the Quantum-Classical Relation*.
- Bokulich, A. (2017). Models and explanation. *Springer handbook of model-based science*, 103–118.
- Bondarenko, A. S. and R. Tempelaar (2023). Overcoming positivity violations for density matrices in surface hopping. *The Journal of Chemical Physics* 158(5).
- Born, M. (1951). Nachr. akad. wiss. göttingen. math-phys. klasse iia. *Math Phys Chem Abt, S Art Nr 6*, 1–3.
- Born, M. and K. Huang (1954). *Dynamical theory of crystal lattices*. Oxford: Clarendon.

- Born, M. and J. R. Oppenheimer (2000, March). On the quantum theory of molecules. In T. S. M. Blinder (Ed.), *Quantum Chemistry*, pp. 1–24. World Scientific.
- Boucher, W. and J. Traschen (1988). Semiclassical physics and quantum fluctuations. *Physical Review D* 37(12), 3522.
- Butterfield, J. (2011). Less is different: Emergence and reduction reconciled. *Foundations of physics* 41, 1065–1135.
- Cartwright, N. (2022). *A Philosopher Looks at Science*. Cambridge University Press.
- Chang, H. (2015). Reductionism and the relation between chemistry and physics. *Relocating the history of science: Essays in honor of Kostas Gavroglu*, 193–209.
- Claverie, P. and S. Diner (1980). The concept of molecular structure in quantum theory: interpretation problems. *Israel Journal of Chemistry* 19(1-4), 54–81.
- Crespo-Otero, R. and M. Barbatti (2018). Recent advances and perspectives on nonadiabatic mixed quantum–classical dynamics. *Chemical reviews* 118(15), 7026–7068.
- Cuffaro, M. E. and S. Hartmann (2021). The open systems view. *arXiv preprint arXiv:2112.11095*.
- Dawid, R. and K. P. Thébault (2015). Many worlds: decoherent or incoherent? *Synthese* 192, 1559–1580.
- Fortin, S. and O. Lombardi (2021). Is the problem of molecular structure just the quantum measurement problem? *Foundations of Chemistry* 23(3), 379–395.
- Franklin, A. (2024). Incoherent? no, just decoherent: how quantum many worlds emerge. *Philosophy of Science* 91(2), 288–309.
- Franklin, A. and V. A. Seifert (2020). The problem of molecular structure just is the measurement problem.
- Gay-Balmaz, F. and C. Tronci (2023). Dynamics of mixed quantum–classical spin systems. *Journal of Physics A: Mathematical and Theoretical* 56(14), 144002.
- González, J. C. M., S. Fortin, and O. Lombardi (2019). Why molecular structure cannot be strictly reduced to quantum mechanics. *Foundations of Chemistry* 21, 31–45.
- Hendry, R. F. (1998). Models and approximations in quantum chemistry. *Poznan Studies in the Philosophy of the Sciences and the Humanities* 63, 123–142.
- Hendry, R. F. (2006). *Is there downward causation in chemistry?* Springer.
- Hendry, R. F. (2010a). Emergence vs. reduction in chemistry. *Emergence in mind*, 205–221.

- Hendry, R. F. (2010b). Ontological reduction and molecular structure. *Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics* 41(2), 183–191.
- Hendry, R. F. (2017). Prospects for strong emergence in chemistry. In *Philosophical and scientific perspectives on downward causation*, pp. 146–163. Routledge.
- Hettema, H. (2017). The union of chemistry and physics. *Cham: Springer International*.
- Huggett, N. and K. P. Thébault (2023). Finding time for wheeler-dewitt cosmology. *arXiv preprint arXiv:2310.11072*.
- Jecko, T. (2014). On the mathematical treatment of the born-oppenheimer approximation. *Journal of Mathematical Physics* 55(5), 053504.
- Joos, E., H. D. Zeh, C. Kiefer, D. J. Giulini, J. Kupsch, and I.-O. Stamatescu (2013). *Decoherence and the appearance of a classical world in quantum theory*. Springer Science & Business Media.
- Ladyman, J. and K. P. Thébault (2024). Open systems and autonomy. <https://philsci-archive.pitt.edu/23701/>.
- Lombardi, O. and M. Castagnino (2010, Oct). Matters are not so clear on the physical side. *Foundations of Chemistry* 12(2), 159–166.
- Lombardi, O. I. (2023). Pragmatic realism in chemistry. *Cogency: Journal of Reasoning & Argumentation* 15, 104–119.
- Messiah, A. (1962). *Quantum mechanics: volume II*. North-Holland Publishing Company Amsterdam.
- Miller, R. (2023). Chemical reduction and quantum interpretation: A case for thomistic emergence. *Foundations of Chemistry* 25(3), 405–417.
- Palacios, P. (2022). *Emergence and Reduction in Physics*. Cambridge University Press.
- Reed, M. and B. Simon (1978). *IV: Analysis of Operators*, Volume 4. Elsevier.
- Rosaler, J. (2015). “formal” versus “empirical” approaches to quantum–classical reduction. *Topoi* 34(2), 325–338.
- Scerri, E. (2024a). The born-oppenheimer and its role in the reduction of chemistry. *Foundations of Chemistry*. unpublished.
- Scerri, E. (2024b). The born-oppenheimer approximation and its role in the reduction of chemistry. (*draft*).
- Scerri, E. R. (2012). Top-down causation regarding the chemistry–physics interface: a sceptical view. *Interface Focus* 2(1), 20–25.

- Seifert, V. A. (2020). The strong emergence of molecular structure. *European Journal for Philosophy of Science* 10(3), 45.
- Seifert, V. A. (2022). Do molecules have structure in isolation? how models can provide the answer. In *Philosophical Perspectives in Quantum Chemistry*, pp. 125–143. Springer.
- Sibaev, M., I. Polyak, F. R. Manby, and P. J. Knowles (2020). Molecular second-quantized hamiltonian: Electron correlation and non-adiabatic coupling treated on an equal footing. *The Journal of Chemical Physics* 153(12).
- Steeger, J. and B. H. Feintzeig (2021). Is the classical limit “singular”? *Studies in History and Philosophy of Science* 88, 263–279.
- Sutcliffe, B. T. and R. G. Woolley (2005). Comment on ‘molecular structure in non-born–oppenheimer quantum mechanics’. *Chemical physics letters* 408(4-6), 445–447.
- Sutcliffe, B. T. and R. G. Woolley (2012). On the quantum theory of molecules. *The Journal of chemical physics* 137(22).
- Torretti, R. (2000). ‘scientific realism’and scientific practice. In *The reality of the unobservable: Observability, unobservability and their impact on the issue of scientific realism*, pp. 113–122. Springer.
- Tully, J. C. (1991). Nonadiabatic molecular dynamics. *International Journal of Quantum Chemistry* 40(S25), 299–309.
- Villaveces C, J. L. and E. E. Daza C (1990). On the topological approach to the concept of chemical structure. *International Journal of Quantum Chemistry* 38(S24), 97–106.
- Wallace, D. (2012). *The emergent multiverse: Quantum theory according to the Everett interpretation*. Oxford University Press, USA.
- Woolley, R. and B. Sutcliffe (1977). Molecular structure and the born—oppenheimer approximation. *Chemical Physics Letters* 45(2), 393–398.
- Woolley, R. G. (1978). Must a molecule have a shape? *Journal of the American Chemical Society* 100(4), 1073–1078.
- Woolley, R. G. (1998). Is there a quantum definition of a molecule? *Journal of Mathematical Chemistry* 23(1), 3–12.
- Yang, Y., H. Ren, M. Zhang, S. Zhou, X. Mu, X. Li, Z. Wang, K. Deng, M. Li, P. Ma, et al. (2023). H₂ formation via non-born-oppenheimer hydrogen migration in photoionized ethane. *Nature Communications* 14(1), 4951.

Yarkony, D. R. (2012). Nonadiabatic quantum chemistry: Past, present, and future. *Chemical reviews* 112(1), 481–498.