



Concerning the question: does quantum mechanics predict molecular structure? An examination of the energetics

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Abstract

There is a controversy concerning the role of the Born-Oppenheimer approximation (BOA) in quantum chemistry molecular orbital calculations. Some philosophers argue that because the BOA *clamps* the position of the nuclei in space the BOA *fixes* the outcome of the calculation, thus calling into question the calculation's legitimacy. As a contribution to the debate, we perform a thermochemical analysis to determine the absolute energies of the quantum Hamiltonian operator, $\hat{H}\psi$, in kJmol^{-1} , with respect to the constitutional isomers ethanol and dimethyl ether and their constituent particles. Our results show that the difference between the quantum Hamiltonian enthalpies, the $\Delta_{\text{QH}}H$, is tiny: $-407,023 \text{ kJmol}^{-1}$ vs. $-407,116 \text{ kJmol}^{-1}$, a 0.02% difference. This is far smaller than the $\sim 1\%$ chemical error deemed acceptable/tolerable in many chemical procedures and calculations.

Keywords Quantum Hamiltonian · Born-Oppenheimer approximation · Molecular orbital theory · Molecular structure · Enthalpy cycles · Chemical error

Introduction

The Coulomb Hamiltonian operator, Eq. (1), for a molecular system, $\hat{H}$, incorporates the potential and kinetic energies of the nuclei and electrons associated with the molecular (multi-particle) Schrödinger wave equation. Solving the Schrödinger wave equation generates a corresponding potential energy surface (PES).

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$$\begin{aligned}
 \hat{H} = & \underbrace{-\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2}_{\text{Electron kinetic Energy } (T_e)} + \underbrace{-\sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2}_{\text{Nuclear kinetic Energy } (T_N)} + \underbrace{\sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{Electron-electron repulsion } (V_{ee})} \\
 & + \underbrace{\sum_{A < B} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|}}_{\text{Nuclear-nuclear repulsion } (V_{NN})} - \underbrace{\sum_{i,A} \frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|}}_{\text{Electron-nucleus repulsion } (V_{en})}
 \end{aligned} \quad (1)$$

In this paper, we look at the often considered pair of constitutional isomers associated with the molecular formula $\text{C}_2\text{H}_6\text{O}$ (9 atomic nuclei and 26 electrons), which corresponds to *either* dimethylether, CH_3OCH_3 , *or* ethanol, $\text{CH}_3\text{CH}_2\text{OH}$. These molecules have the same Hamiltonian, Eq. (1), are described by the same Schrödinger wave equation (Schrödinger, 1935), and appear as two local minima on the resulting PES, Fig. 1.

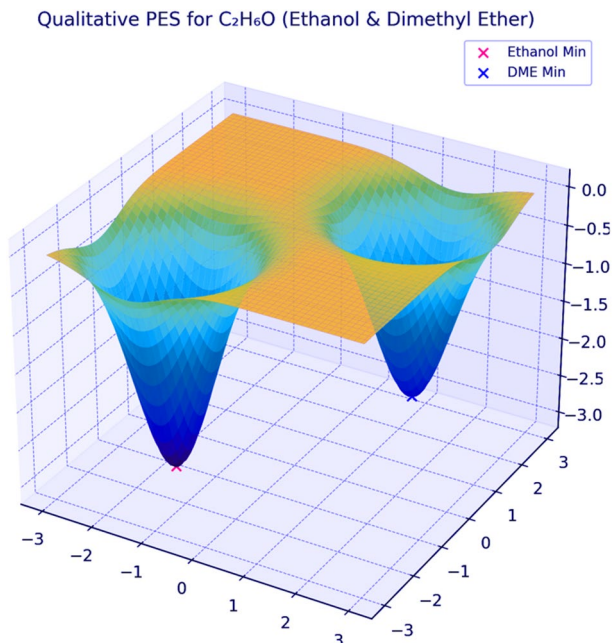
Born and Oppenheimer suggested that a molecular wavefunction, $\Psi(e, N)$, can be written as the product of the electronic, $\Psi(e)$, and nuclear, $\Phi(N)$, component wave-functions (Born & Oppenheimer, 1927), Eq. (2):

$$\Psi(e, N) = \Psi(e) \Phi(N) \quad (2)$$

The full molecular Hamiltonian, H , can be written as the sum of the nuclear kinetic energy, T_N , plus the electronic Hamiltonian, H_e , Eq. (3):

$$H = T_N + H_e \quad (3)$$

Fig. 1 A qualitative potential energy surface (PES) for $\text{C}_2\text{H}_6\text{O}$. The two local minima correspond to ethanol and dimethylether, the only two possible (stable) constitutional isomers. The units of the x, y geometry, and z energy axes are arbitrary. This three dimensional surface includes both $\text{C}_2\text{H}_6\text{O}$ isomers as well as all their possible vibrational and rotational modes



The exact electronic-nuclear wavefunction, the Born–Huang expansion (Born & Huang, 1956) comes from inserting Eq. (3) into molecular Schrödinger equation and expanding the solution in electronic eigenfunctions, Eq. (4):

$$\Psi(e, N) = \sum_k \Psi_k(e; N) \varphi_k(N) \quad (4)$$

The rest mass of a hydrogen nucleus, a single proton, is 1.0072 amu. This is some 1835 times heavier than an electron's rest mass (5.49×10^{-4} amu), and most nuclei are at least an order of magnitude heavier than H-1: carbon-12 = 12.000 amu, oxygen-16 = 15.999 amu, chlorine-35 = 34.968 amu, etc. As atomic nuclei are so much heavier than electrons, $M_A \gg m_e$, they move correspondingly slowly. Thus, most molecular orbital (MO) calculation methodologies adopt the Born–Oppenheimer approximation (BOA), which involves ‘clamping’ the nuclear positions (treating $\mathbf{R}_A$ in Eq. (1) as fixed) and then solving the *electronic* Schrödinger wave equation, Eq. (5):

$$\hat{H}_e \psi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R}) \psi_e(\mathbf{r}; \mathbf{R}) \quad (5)$$

The philosopher's take

There is a belief amongst philosophers of chemistry that quantum theory does not predict molecular structure (Sutcliffe & Woolley, 2012). Robin Hendry, a philosopher of science and chemistry and a well-known commentator on these matters, writes (Hendry, 2022):

“We cannot directly solve the molecular Schrödinger equations, and so must introduce approximations. But it is hard to see the Born–Oppenheimer approximation as a mere approximation if it changes the scope of the quantum-mechanical description, making it apply only to one isomer rather than to all of them... The molecular structures could not, in principle, be explained without them. Hence the different structures, their different symmetry properties and the different causal powers they ground, are effectively introduced as unexplained explainers unless we regard the [quantum] adiabatic separability of the nuclear and electronic motions and the localization of the nuclei as part of the explanation.”

From another book chapter (Hendry, 2024):

“Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and dimethylether (CH_3OCH_3) share the same Schrödinger equation (Sutcliffe & Woolley, 2012). The starting point of the explanation – the molecular Schrödinger equation – does not respect the differences between isomers, and what results from localising the nuclei within the [quantum] adiabatic approximation does respect these differences, so localising the nuclei in positions corresponding to the different isomers effectively inserts these differences.

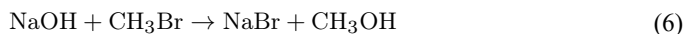
“Reductionists may see this move as having a pragmatic justification: we cannot directly solve the molecular Schrödinger equations, and so must introduce approximations. But it is hard to see the Born-Oppenheimer approximation as a mere approximation if it changes the scope of the quantum-mechanical description, making it apply only to one isomer rather than to all of them. In my first (Hendry, 1998) paper on these topics I argued... that defences of Born-Oppenheimer models based on the proxy view must fail because they change symmetry properties, which are explanatorily relevant features with respect to which isomers may differ, and cannot therefore be grounded in the molecular Schrödinger equation alone. [However], it seems hard to argue that the approximations have no independent explanatory power. The molecular structures could not, in principle, be explained without them. Hence the different structures, their different symmetry properties and the different causal powers they ground, are effectively introduced as unexplained explainers unless we regard the [quantum] adiabatic separability of the nuclear and electronic motions and the localization of the nuclei as part of the explanation. The transformation of nuclei from entities that obey quantum statistics into localized, semi-classical entities would seem to be a good example of transformational emergence.”

Hendry unambiguously restates the philosophical position that molecular structure, with respect to quantum mechanics and the Schrödinger equation, is dependent upon the BOA ‘fixing’ the structure. Furthermore, philosophers point out that the essential feature of the BOA – the separation of nuclear and electronic terms Eqs. (2), (3) and (4) – is not exact because there exists a continuous spectrum of coupling terms (Sutcliffe & Woolley, 2012) (Lombardi, 2025). Thus, the PES is “constructed” and does not naturally emerge from the full Coulomb Hamiltonian, Eq. (1). Several prominent philosophers have gone further and suggested that the BOA violates the Heisenberg Uncertainty Principle, although a recent paper by Scerri has disputed this view (Scerri, 2025).

Our reading of the philosophical position: If we pre-position the nuclei to give dimethylether, we get dimethylether, and if we pre-position the nuclei to give ethanol, we get ethanol. Thus, it is not quantum theory that is generating the constitutional isomers, it is the BOA pre-positioning/clamping the nuclei. This consequentially raises rather deep questions about the science of chemistry and its relationship with its foundational theory, quantum mechanics.

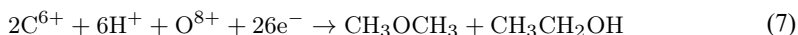
The chemist’s take

Chemists are concerned with energetics and mechanism at the molecular level. *Why* does a particular chemical process occur, and *how* does it occur? The *why* question always concerns the associated energy changes. The *how* question concerns the *atom-to-atom mappings*; how the atoms, ions and electrons move with respect to each other during a reaction. An example: Sodium hydroxide reacts with bromomethane to give sodium bromide and methanol, Eq. (6):



Why does this reaction occur? Because the reaction is exothermic, the products are more stable than the reactants. Energetically, the reaction runs ‘downhill’. Using a more sophisticated Gibbs’ analysis, the free energy, ΔG , of the process is negative. *How* does the reaction occur? Kinetic studies show the reaction process is second order: $\text{rate} = k[\text{CH}_3\text{Br}][\text{HO}^-]$. Experiments with chiral centres demonstrate that there is ‘backside’ attack by the hydroxide ion nucleophile at the $\delta^+\text{C}$ centre, followed by a Walden inversion. Based on this evidence, the mechanism is classified as an $\text{S}_{\text{N}}2$ (substitution, nucleophilic, second order) process.

So, how should chemists approach the dimethyl ether or ethanol issue? The molecular formula, $\text{C}_2\text{H}_6\text{O}$, tells us that we have two carbon nuclei, six hydrogen nuclei, one oxygen nucleus, and 26 electrons. These 35 particles interact to give two possible molecular structures that are constitutional isomers of each other, Eq. (7).



To study this process, we will look at the energies involved using enthalpy cycles. A mechanistic analysis is more challenging due to the artificial nature of the reaction(s), as will be discussed using a *gedankenexperiment*.

Molecular orbital (MO) theory & calculation

MO theory employs the notion that molecules are *atoms with two or more nuclei*. Electrons associate with these multi-nucleated entities using the same rules as they do with single-nucleus atoms. Electrons enter the lowest energy molecular orbital (MO) first, according to the Aufbau principle. MOs can contain a maximum of two electrons, which must be of opposite spin, according to the Pauli Exclusion Principle. When MOs are degenerate (equal energy), maximum multiplicity is observed, according to Hund’s rule.

An idealised MO theory considers that we start with the nuclei, then add electrons to the molecular orbitals, one at a time, until the molecule or molecular ion is constructed, as shown in Fig. 2, which shows the formation of the H_2 molecule. There is, however, a problem with this approach: *the positively charged nuclei will repel each other before any electrons are added*. This is not the situation with atoms, where the atomic nuclei are highly stable entities held together by the strong nuclear force; indeed, atoms can be ionised all the way to the bare nuclei, H^+ , C^{6+} , O^{8+} , etc.

A more pragmatic methodology, used by most computer code, is to employ the linear combination of atomic orbital (LCAO) approach, where neutral atoms have their atomic orbitals *morphed* into molecular orbitals by linear combination, Fig. 3. (The AOs contract and deform radially, and they modify their angular shapes by mixing *p*-valence orbitals with *d* and *f* functions, using so-called ‘poly-polarized basis sets’.) It transpires that atomic and molecular orbital phase symmetry arguments not only allow this approach, but they also greatly reduce computational time. As the atoms in the proto-molecule are neutral, the issue of nuclear repulsion associated with bare nuclei is removed.

Computer code generally operates via the sequence as shown in Fig. 4. A first guess at a molecular structure is made, with the nuclei clamped into position, as per the Born-Oppenheimer approximation. The overall energy is calculated using the chosen method or methods. The positions of the nuclei are adjusted, using the mathematics of variational

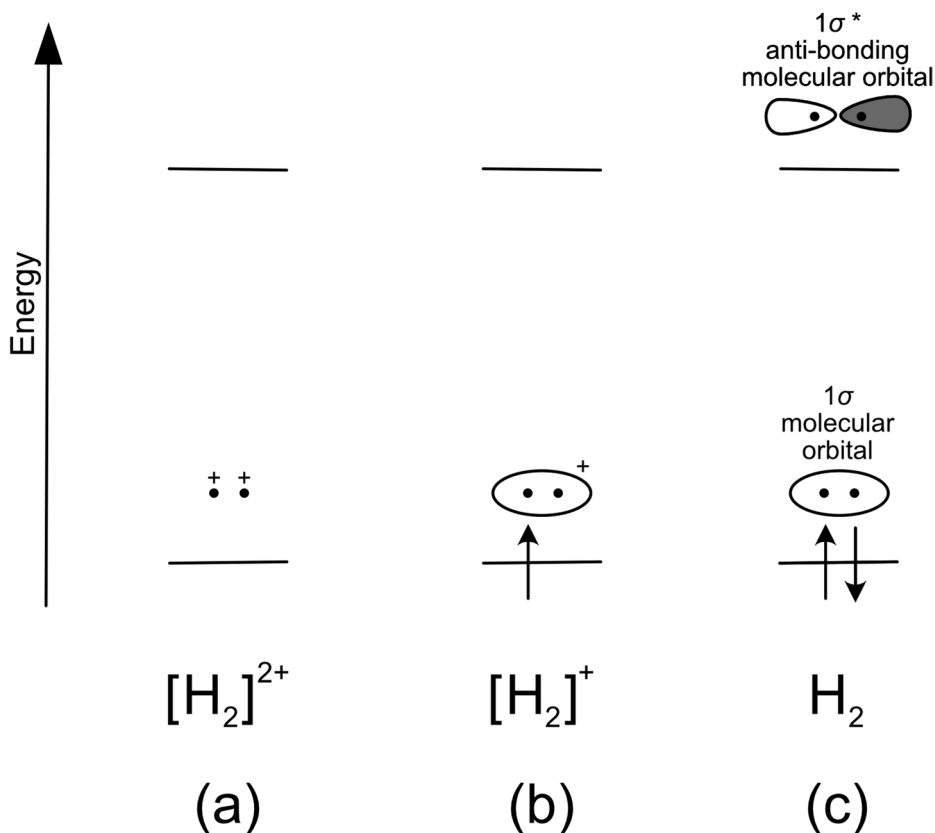


Fig. 2 In the idealised molecular orbital approach to forming hydrogen, H_2 . Two hydrogen nuclei are placed in space (a), giving a hypothetical $[H_2]^{2+}$ ion. The electrons are added one at a time, first to form (b) the $[H_2]^+$ ion – the simplest possible molecular ion and of great theoretical importance – and then the neutral H_2 molecule (c) is formed. The 1σ MO of the H_2 molecule is bonding and is the highest occupied molecular orbital or HOMO. The next molecular orbital in terms of energy is $1\sigma^*$ MO which is anti-bonding it is lowest unoccupied molecular orbital or LUMO

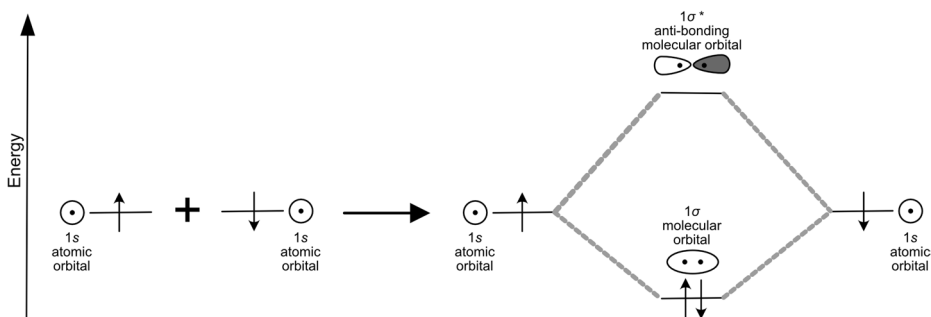


Fig. 3 An alternative approach for forming the hydrogen molecule, H_2 , is to take two hydrogen atoms, each with one electron in their $1s$ atomic orbitals. The orbitals can be combined using the linear combination of atomic orbitals (LCAO) approach, where the two $1s$ AOs overlap and combine to give the 1σ MO

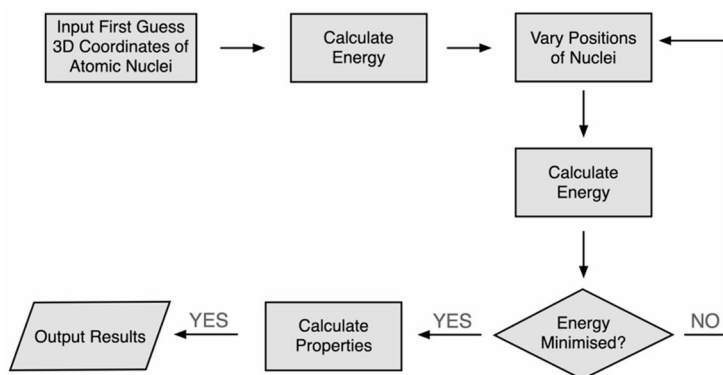


Fig. 4 Calculation involves finding the minimum energy of the molecular system under investigation. The positions of the nuclei are altered, using variational calculus, and calculations of the energy performed until the nuclei are in positions that give the lowest energy

calculus, re-clamped, and the energy recalculated. This process is repeated. After a sequence of between 5 and 100 iterations, and the nuclei are deemed to be in positions that give the lowest overall energy to the electronic molecular structure, the energy minimisation part of the computer code is finished. Thus, the Born-Oppenheimer approximation is a crucial feature/assumption of most quantum chemistry molecular structure software.

Once the energy is deemed to be minimised, the code generates and outputs the results: bond lengths, bond angles, MO energies, geometries, van der Waals surface, polarity, prediction of infrared spectra, FMO geometries, etc. Figure 5 shows the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of dimethyl ether and ethanol, our two molecules of interest, Fig. 5.

There are fundamental difficulties with all types of molecular orbital calculation.

- Only two particle systems can be solved analytically, and there are only a few two-particle systems of chemical interest: the hydrogen atom, H^- ; the helium cation, He^+ ; the lithium dication, Li^{2+} ; beryllium trication, Be^{3+} ; etc. For all other atomic and molecular systems, approximations must be made.
- The Schrödinger wave equation gives a non-relativistic description of the electron's behaviour in a molecule. Spin-orbit coupling is not considered; there is no quantum electrodynamical (QED) level of analysis; fields are not quantised, etc.
- Hartree–Fock (HF) molecular orbital calculations are foundational in quantum chemistry, but they involve significant approximations and limitations. For example, HF treats each electron as moving in the average field created by all other electrons, so it neglects static and dynamic electron correlations. There are no real-time, mutual adjustments of electrons avoiding each other due to Coulomb repulsion. So called “post-HF methods” deal with some of these HF limitations. The HF orbital approximation is too crude for most chemical approximations, it must be improved so that correlation is approximately considered by using some Kohn–Sham approximation, at least.
- Molecular orbital calculations are always a balance between obtaining *good enough* results and computer time. If a non-relativistic Schrödinger equation is being used in the computer model, there is little point in running the iterative cycles (Fig. 4) past the

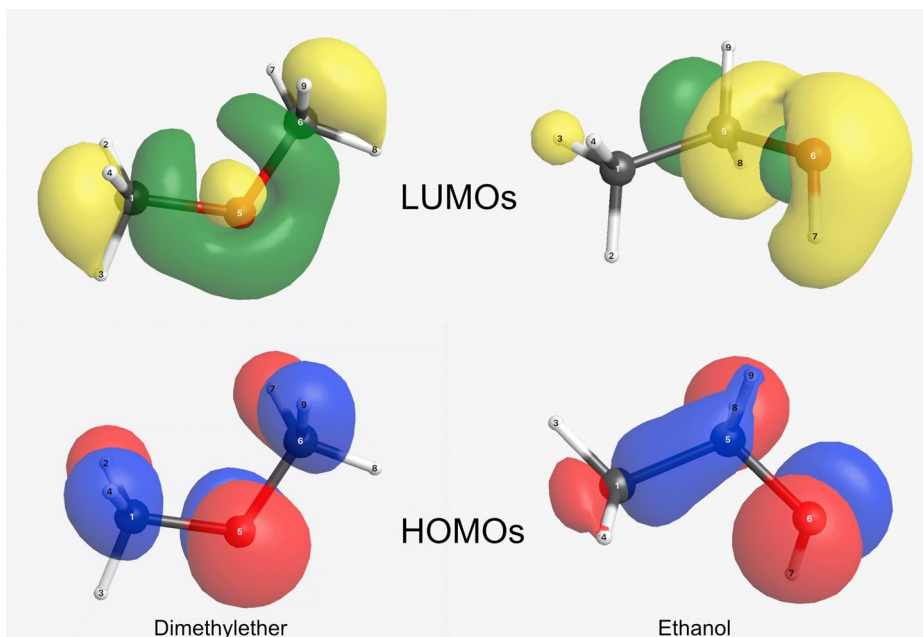


Fig. 5 The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of dimethyl ether and ethanol, as calculated by a semiempirical MOPAC calculation using <https://www.webmo.net>. The differential colours (red and blue in the HOMOs and green and yellow in the LUMOs) represent orbital phase. Note how different the frontier molecular orbitals (FMOs) of dimethyl ether and ethanol are: dimethyl ether is symmetrical about the oxygen; ethanol is not

inherent accuracy of the theoretical model in use.

Born-Haber enthalpy cycles

In this paper, we examine the molecular orbital quantum Hamiltonian, $H\psi$, in terms of enthalpy cycles and look at the differential energies involved. Born-Haber cycles should really be called *Born–Haber–Fajans thermochemical correlations* because Born¹, Haber, and Fajans independently published in the same issue of the same journal in 1919 (Born, 1919); (Haber, 1919); (Fajans, 1919).

Enthalpy cycles are a way of exploring the thermochemistry of chemical reaction processes in terms of the energetics of the various steps. The logic of the calculations relies on the Mass and Energy Conservation Laws and Hess's (consequential) Law that the total enthalpy change during a chemical reaction is independent of the sequence in which the steps are taken.

Born-Haber cycles are primarily concerned with calculating the lattice enthalpies, $\Delta_{\text{latt}}H$, of ionic compounds, where the lattice enthalpy corresponds to gas phase positive & negative ions coalescing into an ionic solid, Eq. (8).

¹ (Max) Born of the Born–Oppenheimer approximation is the same person as (Max) Born of the Born-Haber cycle. *Born again*, as we might say.



The lattice enthalpy, $\Delta_{\text{latt}}H$, is an empirical measure of the strength of the ionic bonding in ionic materials. As the bonding in an ionic material is deemed to be purely electrostatic in nature, the $\Delta_{\text{latt}}H$ is therefore a measure of this electrostatic attraction between oppositely charged ions in the bulk material, Fig. 6. The magnitude of the lattice enthalpy, $\Delta_{\text{latt}}H$, is exceedingly useful because it can be used to compare & contrast different ionic compounds and draw conclusions about the properties of the ions involved. Hess's Law states that the sum of all the enthalpy changes in a cycle equals zero; therefore the $\Delta_{\text{latt}}H$, lattice enthalpy, can be determined by simple subtraction, Fig. 7.

Enthalpy cycles can be applied to a wide range of chemical reaction processes; they are a general tool for thermochemical analysis, Fig. 8.

Note that not all computational methods employ the Born-Oppenheimer approximation. Direct quantum chemistry or Electron–Nuclear Dynamics (END) covers a set of methods that avoid the BOA altogether (Öhrn & Deumens, 2002) (Teixeira & Morales, 2020). The technique is used when modelling high-speed atomic collisions, where the nuclear motion may be comparable to, or faster than, the electronic motion (Lader & et al., 2019). Scerri has pointed out that recent Monte Carlo methods do not use the BOA (Scerri, 2025), (Lang, 2024).

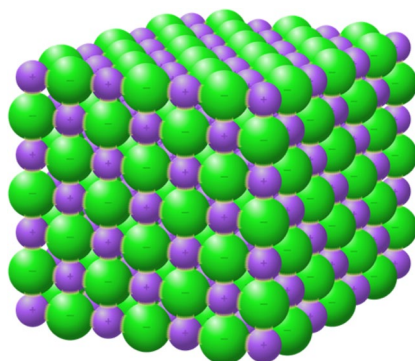
Calculating the enthalpy change of the Quantum Hamiltonian, $\Delta_{\text{QH}}H$, for H_2

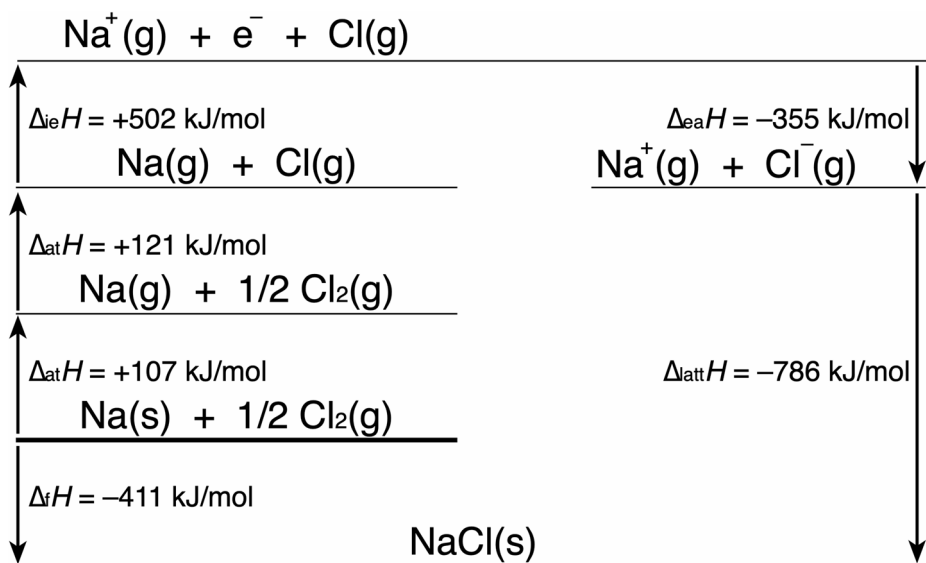
The $\hat{H}\psi$ for hydrogen, H_2 , involves adding two H^+ nuclei and two electrons, Eq. (1), to form the H_2 molecule. We can consider this as a thermochemical enthalpy cycle, Fig. 9.

Note that while chemists tend to work in units of kJmol^{-1} , physicists prefer to use units of electron volts, eV, per particle. However, it is simple to convert from kJmol^{-1} to the electron volt 'per particle' description: The $H_2(g)$ $\Delta_{\text{QH}}H = -3060 \text{ kJmol}^{-1} = -31.715 \text{ eV}$ (per H_2 particle).

There are a couple of interesting mechanistic ('how') details that are not addressed with the overall equation. Would the reaction proceed directly, as per Eq. (9)? This would be most unlikely, as four particles would have to move simultaneously.

Fig. 6 An ionic compound like sodium chloride has a face-centred cubic crystal structure, where each sodium (Na^+) ion is surrounded by six chloride (Cl^-) ions, and each chloride ion is surrounded by six sodium ions. There is electrostatic bonding between the oppositely charged ions in the solid ionic material, but not explicit atom-to-atom or ion-to-ion bonds. Image: NaCl_bonds.svg CC BY-SA 4.0. Attribution: Goran tek-en





$$\Delta_{\text{f}}H + \Delta_{\text{at}}H + \Delta_{\text{at}}H + \Delta_{\text{ie}}H + \Delta_{\text{ea}}H + \Delta_{\text{latt}}H = 0$$

SO:

$$\Delta_{\text{f}}H + \Delta_{\text{at}}H + \Delta_{\text{at}}H + \Delta_{\text{ie}}H + \Delta_{\text{ea}}H = -\Delta_{\text{latt}}H$$

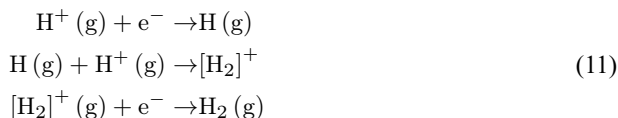
Fig. 7 Born-Haber enthalpy cycles can be used to determine the experimentally inaccessible, but interesting, lattice enthalpy, $\Delta_{\text{latt}}H$, value



The reaction would likely proceed in a stepwise manner, producing hydrogen atoms first and then have these react to form H_2 , Eq. (10).



Alternatively, the reaction could proceed via the single-electron $[\text{H}_2]^+$ molecular ion, Eq. (11).



However, it is not necessary to consider the mechanistic process due to Hess' Law which tells us that the overall energetics are the same, whatever the mechanistic route.

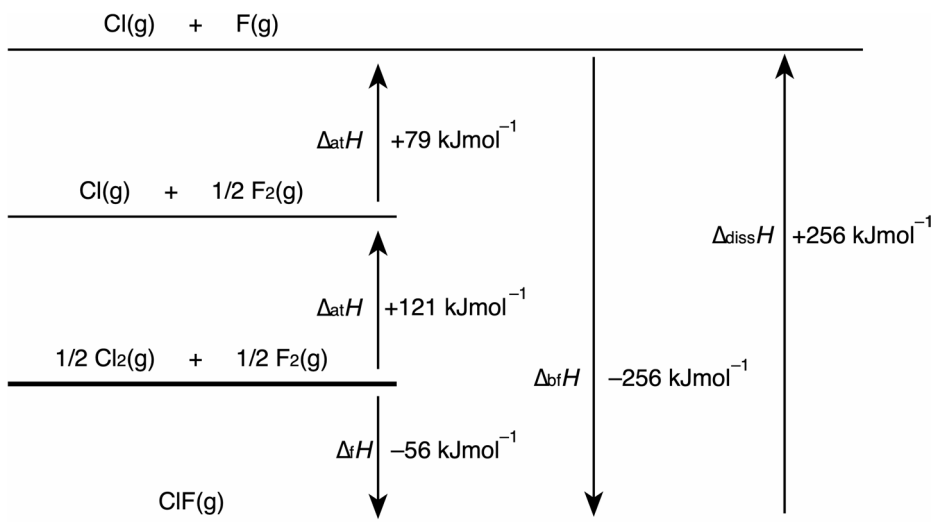


Fig. 8 The strength of the Cl–F bond in chlorine fluoride can be calculated from the enthalpy of formation of chlorine fluoride ($\Delta_f H = -56 \text{ kJmol}^{-1}$), the enthalpy of atomisation of chlorine ($\Delta_{\text{at}} H = +121 \text{ kJmol}^{-1}$), and the enthalpy of atomisation of fluorine ($\Delta_{\text{at}} H = +79 \text{ kJmol}^{-1}$). The bond formation enthalpy, $\Delta_{\text{bf}} H$ will therefore be -256 kJmol^{-1} . However, bond strength is normally considered as the energy to break or dissociate a bond (the opposite of bond formation), so the bond dissociation enthalpy, $\Delta_{\text{diss}} H$, will be $+256 \text{ kJmol}^{-1}$

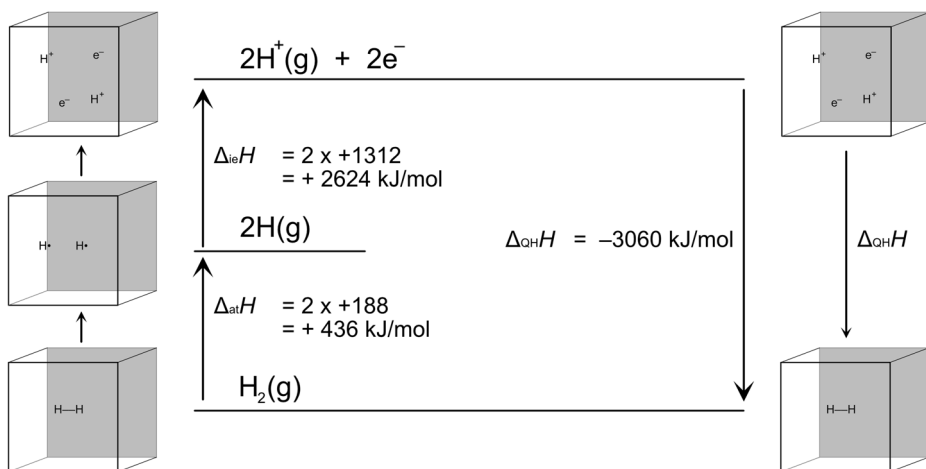


Fig. 9 Enthalpy cycle to calculate the energy of the quantum Hamiltonian, $\hat{H}\psi$, here designated $\Delta_{\text{QH}} H$. The hydrogen molecule, $\text{H}_2(\text{g})$, is atomised into two hydrogen atoms, $2 \text{H}(\text{g})$. These are then ionised into two gas phase protons and two electrons, $2 \text{H}^+(\text{g}) + 2\text{e}^-$. The enthalpy cycle tells us that then these interact to form $\text{H}_2(\text{g})$, the enthalpy change, $\Delta_{\text{QH}} H$, is -3060 kJmol^{-1}

There is also the issue of nuclear and electron spin, which is particularly important with hydrogen atoms and molecules.

- Doubly spin polarised atomic hydrogen atoms, nuclear spin ($\uparrow$) and electron spin ($\uparrow$), cannot react to form diatomic H_2 because the reaction process is symmetry forbidden in that energy and spin cannot change simultaneously. Indeed, doubly spin-polarised atomic hydrogen is stable at low Kelvin temperatures for long periods (Shinkoda & Hardy, 1991).
- The $H_2(g)$ molecule can exist as two nuclear spin isomers: *ortho*- H_2 ($\uparrow\uparrow$), and *para*- H_2 ($\uparrow\downarrow$). At 298 K and at thermal equilibrium, thermal excitation causes hydrogen to consist of approximately 75% orthohydrogen and 25% parahydrogen.

Constitutional isomers: dimethyl ether & ethanol

We can calculate the $\Delta_{QH}H$ for the formation of dimethylether, CH_3OCH_3 , and compare the value with the $\Delta_{QH}H$ for the formation of ethanol, CH_3CH_2OH , Fig. 10. To calculate the $\Delta_{QH}H$ values, Eq. (7), it is necessary to atomise and ionise two carbon atoms from their standard solid state, $C(s)$, to the bare nuclei, $2 C^{6+}(g)$ ions plus 12 electrons, an oxygen atom from its standard gaseous state, $1/2 O_2(g)$, to a bare $O^{8+}(g)$ ion plus 8 electrons, and three $H_2(g)$ molecules to 6 bare $H^+(g)$ ions plus 6 electrons.

Ionisation energy values are determined experimentally using UV light of specific wavelengths to eject the electrons. As the wavelength of light can be measured with high precision, the various ionisation energies: $C(g)$ to $C^{6+}(g)$, $O(g)$ to $O^{8+}(g)$, and $H(g)$ to $H^+(g)$ are, correspondingly, known to high precision, usually to 4 or 5 significant figures. Furthermore, all but one of the steps in the $\Delta_{QH}H$ calculation for dimethyl ether are *identical* to the steps in the $\Delta_{QH}H$ calculation for ethanol. The exceptions are the two enthalpy of formation, $\Delta_f H$, steps, $-184.01 \text{ kJmol}^{-1}$ for dimethyl ether and $-277.05 \text{ kJmol}^{-1}$ for ethanol. Thus, should there be any errors in the large ionisation energy values of the atoms involved, these will cancel out between the two calculations, giving high confidence in the overall differential energy result.

The results of the $\Delta_{QH}H$ calculations are as follows:

$$\text{Dimethyl ether } D_{QH}H = -407,023 \text{ kJ mol}^{-1} (-4218.22\text{eV})$$

$$\text{Ethanol } D_{QH}H = -407,116 \text{ kJ mol}^{-1} (-4219.18\text{eV})$$

Thus, ethanol (liquid) is $-93.04 \text{ kJmol}^{-1}$ (-0.9643 eV) more stable than dimethyl ether (gas). This equates to a 0.02% difference in the $\Delta_{QH}H$ values between the two molecules with respect to their isolated fully ionised nuclei and electrons, Eq. (7). The two energy minima in the potential energy surface, Fig. 1, have almost the same depth.

Consider the process described in Eq. (7) as a *gedankenexperiment* (thought experiment), Fig. 11. We have a tiny magnetic confinement container (a nano box) holding a plasma of $2C^{6+}(g)$, $1O^{8+}(g)$, $6H^+(g)$ and $26e^-$ electrons. This state corresponds to the Coulomb Hamiltonian operator, $\hat{H}$, Eq. (1). The 35 particles coalesce to dimethyl ether and/or ethanol in

Enthalpy change of the Dimethyl ether (DME) Quantum Hamiltonian

 $\Delta_{\text{QH, DME}} H = -407023 \text{ kJ mol}^{-1}$

	Enthalpy	Stoichiometry
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}^+(\text{g}) \quad \text{O}^{8+}(\text{g}) \quad 26 \text{ e}^-$	$\Delta_{\text{QH}} H$	
Ionisation of H	$\Delta_{\text{ion, H}} H$	1312 6
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ }^+\text{H}(\text{g}) \quad \text{O}^{8+}(\text{g}) \quad 20 \text{ e}^-$		
8th ionisation of O	$\Delta_{\text{ion, O}} H$	84,078 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{7+}(\text{g}) \quad 19 \text{ e}^-$		
7th ionisation of O	$\Delta_{\text{ion, O}} H$	71,330 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{6+}(\text{g}) \quad 18 \text{ e}^-$		
6th ionisation of O	$\Delta_{\text{ion, O}} H$	13,327 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{5+}(\text{g}) \quad 17 \text{ e}^-$		
5th ionisation of O	$\Delta_{\text{ion, O}} H$	10,990 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{4+}(\text{g}) \quad 16 \text{ e}^-$		
4th ionisation of O	$\Delta_{\text{ion, O}} H$	7469 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{3+}(\text{g}) \quad 15 \text{ e}^-$		
3rd ionisation of O	$\Delta_{\text{ion, O}} H$	5301 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{2+}(\text{g}) \quad 14 \text{ e}^-$		
2nd ionisation of O	$\Delta_{\text{ion, O}} H$	3388 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 13 \text{ e}^-$		
1st ionisation of O	$\Delta_{\text{ion, O}} H$	1314 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 12 \text{ e}^-$		
6th ionisation of C	$\Delta_{\text{ion, C}} H$	47,277 2
$2 \text{ C}^{5+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 10 \text{ e}^-$		
5th ionisation of C	$\Delta_{\text{ion, C}} H$	37,831 2
$2 \text{ C}^{4+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 8 \text{ e}^-$		
4th ionisation of C	$\Delta_{\text{ion, C}} H$	6222.7 2
$2 \text{ C}^{3+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 6 \text{ e}^-$		
3rd ionisation of C	$\Delta_{\text{ion, C}} H$	4620.5 2
$2 \text{ C}^{2+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 4 \text{ e}^-$		
2nd ionisation of C	$\Delta_{\text{ion, C}} H$	2352.6 2
$2 \text{ C}^+(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 2 \text{ e}^-$		
1st ionisation of C	$\Delta_{\text{ion, C}} H$	1086.5 2
$2 \text{ C}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g})$		
Atomisation of H	$\Delta_{\text{at, H}} H$	218 6
$2 \text{ C}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g})$		
Atomisation of C	$\Delta_{\text{at, C}} H$	717 2
$2 \text{ C}(\text{s}) \quad 3 \text{ H}_2(\text{g}) \quad \text{O}(\text{g})$		
Atomisation of O	$\Delta_{\text{at, O}} H$	248 1
$2 \text{ C}(\text{s}) \quad 3 \text{ H}_2(\text{g}) \quad \frac{1}{2} \text{ O}_2(\text{g})$		
Formation of dimethyl ether	$\Delta_f H$	-184.01 1
$\text{CH}_3\text{-O-CH}_3(\text{g})$		

DME
 $\Delta_{\text{QH}} H$
-407023
kJ mol⁻¹

Enthalpy change of the Ethanol (EtOH) Quantum Hamiltonian

 $\Delta_{\text{QH, EtOH}} H = -407116 \text{ kJ mol}^{-1}$

	Enthalpy	Stoichiometry
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}^+(\text{g}) \quad \text{O}^{8+}(\text{g}) \quad 26 \text{ e}^-$	$\Delta_{\text{QH}} H$	
Ionisation of H	$\Delta_{\text{ion, H}} H$	1312 6
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{8+}(\text{g}) \quad 20 \text{ e}^-$		
8th ionisation of O	$\Delta_{\text{ion, O}} H$	84,078 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{7+}(\text{g}) \quad 19 \text{ e}^-$		
7th ionisation of O	$\Delta_{\text{ion, O}} H$	71,330 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{6+}(\text{g}) \quad 18 \text{ e}^-$		
6th ionisation of O	$\Delta_{\text{ion, O}} H$	13,327 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{5+}(\text{g}) \quad 17 \text{ e}^-$		
5th ionisation of O	$\Delta_{\text{ion, O}} H$	10,990 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{4+}(\text{g}) \quad 16 \text{ e}^-$		
4th ionisation of O	$\Delta_{\text{ion, O}} H$	7469 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{3+}(\text{g}) \quad 15 \text{ e}^-$		
3rd ionisation of O	$\Delta_{\text{ion, O}} H$	5301 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}^{2+}(\text{g}) \quad 14 \text{ e}^-$		
2nd ionisation of O	$\Delta_{\text{ion, O}} H$	3388 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 13 \text{ e}^-$		
1st ionisation of O	$\Delta_{\text{ion, O}} H$	1314 1
$2 \text{ C}^{6+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 12 \text{ e}^-$		
6th ionisation of C	$\Delta_{\text{ion, C}} H$	47,277 2
$2 \text{ C}^{5+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 10 \text{ e}^-$		
5th ionisation of C	$\Delta_{\text{ion, C}} H$	37,831 2
$2 \text{ C}^{4+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 8 \text{ e}^-$		
4th ionisation of C	$\Delta_{\text{ion, C}} H$	6222.7 2
$2 \text{ C}^{3+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 6 \text{ e}^-$		
3rd ionisation of C	$\Delta_{\text{ion, C}} H$	4620.5 2
$2 \text{ C}^{2+}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 4 \text{ e}^-$		
2nd ionisation of C	$\Delta_{\text{ion, C}} H$	2352.6 2
$2 \text{ C}^+(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g}) \quad 2 \text{ e}^-$		
1st ionisation of C	$\Delta_{\text{ion, C}} H$	1086.5 2
$2 \text{ C}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g})$		
Atomisation of H	$\Delta_{\text{at, H}} H$	218 6
$2 \text{ C}(\text{g}) \quad 6 \text{ H}(\text{g}) \quad \text{O}(\text{g})$		
Atomisation of C	$\Delta_{\text{at, C}} H$	717 2
$2 \text{ C}(\text{s}) \quad 3 \text{ H}_2(\text{g}) \quad \text{O}(\text{g})$		
Atomisation of O	$\Delta_{\text{at, O}} H$	248 1
$2 \text{ C}(\text{s}) \quad 3 \text{ H}_2(\text{g}) \quad \frac{1}{2} \text{ O}_2(\text{g})$		
Formation of ethanol	$\Delta_f H$	-277.05 1
$\text{CH}_3\text{CH}_2\text{OH}(\text{l})$		

EtOH
 $\Delta_{\text{QH}} H$
-407116
kJ mol⁻¹

Fig. 10 Enthalpy cycles for the formation of the two constitutional isomers of $\text{C}_2\text{H}_6\text{O}$: dimethyl ether and ethanol. The steps, from the elements in their standard state, can proceed in two ways: the enthalpy of formation, $\Delta_f H$, or via atomisation and full ionisation to: $2\text{C}^{6+}(\text{g})$, $\text{O}^{8+}(\text{g})$, $6 \text{H}^+(\text{g})$, and 26e^- . The combination of these 35 particles, Eq. (7), corresponds to the quantum Hamiltonian, $\Delta_{\text{QH}} H$, for the formation of dimethyl ether and/or ethanol. All enthalpy data from CRC Handbook of Chemistry and Physics 84th Ed, etc. via Wikipedia (Wikipedia, 2024)

the ratio 0.9998 : 1.0002 (49.989%:50.011%) due to the tiny difference in energy between the two molecules.

It should be noted that there are alternative mechanistic pathways leading to different products, but they are not being considered as part of this *gedankenexperiment*. For example, it is well known that ethanol can undergo elimination to form ethene and water, $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$; the elements may coalesce into their standard states $2 \text{C}(\text{s})$, $3 \text{H}_2(\text{g})$, $1/2 \text{O}_2$; the dicarbon molecule, C_2 , is known, etc. There are many alternative pathways and products. However, Eq. (1) and Eq. (7) only consider the formation of dimethyl ether and/or ethanol.

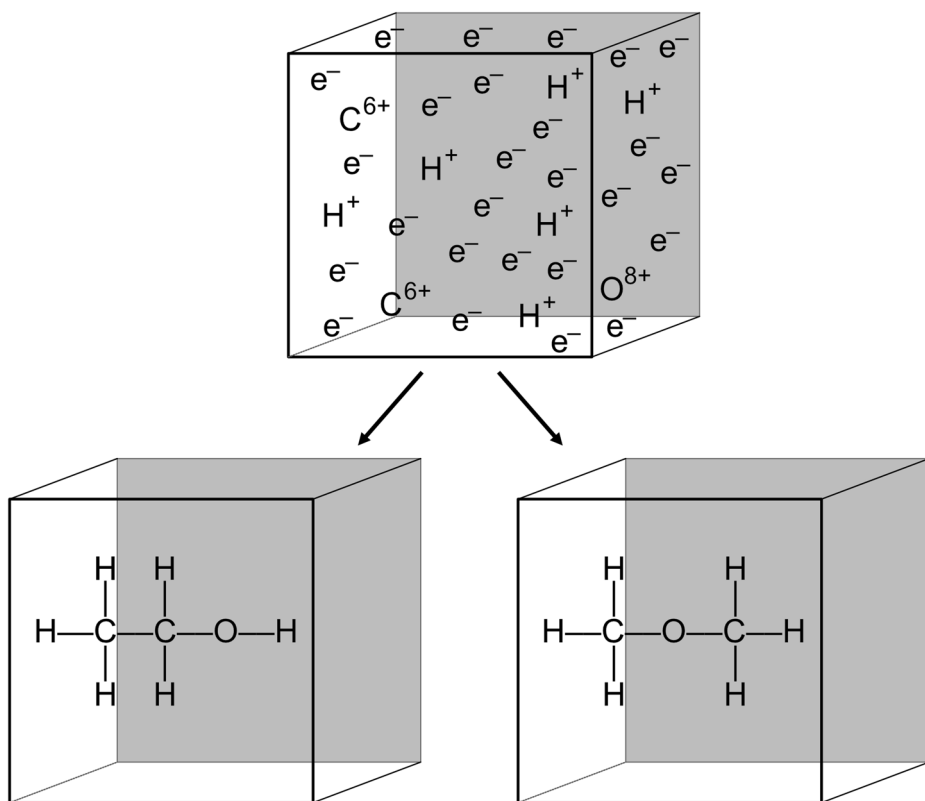


Fig. 11 The process of $2C^{6+}(g)$, $O^{8+}(g)$, $6H^+(g)$ & $26e^-$ electrons, Eq. (7), coalescing to dimethyl ether and/or ethanol in a confined nano-box

Chemical error

Many physical constants are known to extraordinary accuracy and precision. The speed of light, c , is defined as 299,792,458 m/s which is then used to define the metre. The fine structure constant has a value of $\alpha^{-1} = 137.035999084(21)$, where the last two numbers in brackets are uncertain. The atomic masses of individual atoms are known to high accuracy and precision: The H-1 isotope has a mass of 1.00782503207(10)au (atomic units), with respect to the C-12 isotope, which is *defined* as having a mass of exactly 12.0000000000au.

Outside the rarified world of physical constants and individual atomic masses with their 12 significant figures of accuracy, measurements are always subject to error. Elemental carbon is deemed to have a relative average atomic mass of 12.011 due to the natural variation in C-12 vs. C-13 abundance ratios between samples.

In chemistry, we always have sample variation. Thus, if analytical samples vary by $\pm 5\%$ with respect to a particular analyte, why perform the individual analysis steps with $\pm 0.1\%$ precision?

- The United States Pharmacopeia states that a tablet's active ingredient must be $\pm 15\%$ of the value stated on the label (USP, 2006).

- Environmental analytical results may be concerned with orders of magnitude values. For example, copper concentration in pristine river water may vary between 0.5–10 µg/L or 0.1 to 10 ppb (parts per billion); however, the value will inevitably fluctuate between samples taken at different times on different days. Thus, environmental values for Cu concentration may be quoted as “5 ppb”, i.e., a result given to one significant figure.
- Molecular orbital calculations are subject to errors, both in the methodologies used and the requirement to save computer time. Consider bond-length calculations. Typically, Hartree-Fock (HF) calculations show 2–5% errors; density functional theory (DFT) calculations have errors of 1–3% and *gold standard* CCSD(T) calculations give values about 1% compared with experiment (Jensen, 2017), (Mardirossian & Head-Gordon, 2017).

For many reasons, chemical error is usually regarded to be “*about* 1%”, one part in a hundred, although $\pm 5\%$ is often acceptable, depending upon the situation. Most MO calculations fall within $\pm 5\%$ broad range, although computationally expensive techniques can approach 1%.

Summary

1. The BOA clamps nuclei during calculations, but the nuclei *are* moved, using the logic of variational calculus, between iterations until the minimum energy conformation is found, Fig. 4. Critics omit this detail and *imply* that the clamped nuclei do not move at all. Furthermore, harmonic vibration calculations are routinely performed using higher levels of the BO expansion, Eq. (4), once the equilibrium structure has been determined.
2. The difference between the calculated $\Delta_{\text{QH}}H$ for dimethyl ether is 0.02% of the value calculated for ethanol, Fig. 10. This is far smaller than both the 1% “acceptable” chemical error and the error in molecular orbital software calculations.
3. A *gedankenexperiment* consisting of a nano box containing a plasma of $2\text{C}^{6+}(\text{g})$, $\text{O}^{8+}(\text{g})$, $6\text{H}^+(\text{g})$ & 26e^- electrons, Fig. 11, and using the $\Delta_{\text{QH}}H$ data predicts that these particles will coalesce to dimethyl ether and/or ethanol in the ratio 0.9998:1.0002. This ratio is obtained by the particles behaving stochastically.
4. If we wish to perform a molecular orbital calculation on dimethylether, CH_3OCH_3 , it is *simply easier* for all actors – the programmers who write the code, the user of the software, the administrator who has to pay for the compute resources – for the *in silico* model to start with an approximate structure of dimethyl ether and then work to optimise that initially guessed structure. Likewise, for studies of ethanol. Indeed, it would be somewhat unhelpful if the molecular structure software, such as Gaussian or Spartan (two popular commercial packages), reported as their first line of output:

"The Coulomb Hamiltonian operator, $\hat{H}$, for $\text{C}_2\text{H}_6\text{O}$ generates a potential energy surface with two minima that correspond to two constitutional isomers: dimethyl ether and ethanol. Calculations show these will form in the ratio 0.9998:1.0002. Select the isomer you are interested in to generate its properties: bond lengths, IR and NMR spectra, HOMO/LUMO energy levels and diagrams, etc."

With more complicated molecules, there are many possible constitutional and stereoisomers.

- MOLGEN online predicts that there are 79 isomers of molecules containing C, H, O & N with a molecular mass up to 46 (Gugisch, 2016) (Gugisch, 2016).
- Using Pólya's theorem, there are potentially 4,111,846,763 constitutional isomers of $C_{30}H_{62}$, although many will be sterically impossible/inaccessible (Chyzak, 2008).
- Taxol/Paclitaxel has the molecular formula $C_{47}H_{51}NO_{14}$. How many possible constitutional & stereoisomers are there? A trillion? A quadrillion?
- If a researcher is carrying out an in silico study of how morphine binds with the δ -opioid receptor, why would they be interested that the Coulomb Hamiltonian operator, $\hat{H}$, for $C_{17}H_{19}NO_3$ generates a potential energy surface with several million possible minima?

Conclusion

Input from philosophers is often exceedingly useful for scientists.

- Understanding the nature and meaning of the term '*element*' has great practical value. The term '*chlorine*' is ambiguous without context. '*Chlorine*' can refer to the transcendental or *basic substance*, as represented on the periodic table; it can refer to a gas phase chlorine atom, $Cl(g)$; or, it can refer to the diatomic molecular substance, $Cl_2(g)$, which is the form of *chlorine, the simple substance* under standard conditions of 298 K and 100 kPa (1.0 atm and 25 °C). Owners of swimming pools '*add chlorine*' to keep them clean; here the '*chlorine*' is in the form of chlorate(I) ion.
- Chemists frequently simplify their notion of a covalent bond as being a '*flexible rod*' or '*spring*' holding two atoms together, and the use of a dash or line between two atoms, $Cl-Cl$, reinforces this view. Chemists are inclined to use this classical model when teaching non-chemists, even when they are fully aware it is an incorrect oversimplification.
- Rigorous philosophical analysis helps us disentangle the various meanings of the terms like *element*. Likewise, chemists need to bear in mind that chemical bonding is a subtle property, and they should use their analogies wisely.

The aim of this paper is not to explain why there is a philosophical issue with the use of the Born-Oppenheimer approximation with respect to the Coulomb Hamiltonian operator or to resolve the matter in any way. The aim is to put any concerns into context by looking at the energies involved. We can then ask if the thermochemical evidence backs-up or dispels the philosophical anxieties. Should practicing chemists be concerned about using the BOA? Are the philosophical foundational science reservations justified with respect to the BOA?

We hold that the thermochemical evidence presented here show that there are no practical concerns with the use of the Born-Oppenheimer approximation; it is a pragmatic step that allows computational molecular scientists to work on the molecule they wish to work on. Furthermore, when the BOA does not hold, such as when looking at fast molecular collisions, there are computational alternatives available.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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