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Distinguishing between the cause and the result of chemical bonding: insights provided by the virial diagnostic

Charles S. McCaw

csm@wincoll.ac.uk

Winchester College

W. H. Eugen Schwarz

University of Siegen

Research Article

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Posted Date: November 13th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-10832987/v1

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Additional Declarations: Competing interest reported. One of the authors, WHES, is on the Foundations of Chemistry Editorial Board.

Distinguishing between the cause and the result of chemical bonding: insights provided by the virial diagnostic

Charles S. McCaw,*

Winchester College, Winchester, UK; orcid: 0009-0000-1258-0100

W. H. Eugen Schwarz

Department of Chemistry, University of Siegen, Siegen, Germany; Theoretical and Computational Chemistry Center, Tsinghua University, Beijing, China; orcid: 0000-0001-8730-1508

ABSTRACT

The covalent bond-causing mechanism – i.e. the delocalization of valence electrons through the orbital-overlap region – lowers the kinetic energy contribution *in this overlap region*. Yet the virial theorem requires a *total increased positive kinetic energy* of the stable molecule at equilibrium, equal in size to the lowered negative total energy. This (purely apparent) inconsistency is naturally resolved by the *relaxation of the atoms* in the molecule, following the bond-causing mechanism in the overlap region, producing large changes of the kinetic and potential energies in opposite directions, satisfying the virial theorem and causing just a small decrease in the total energy. A simple model is presented to illustrate the requirement for the optimization of an internal parameter of the system to equilibrate and stabilize a molecule energetically. This approach satisfies the virial theorem, often neglected in the discussion of chemical bonding of 'frozen' atoms. And it exemplifies the general mechanism of many common counter-intuitive observations in daily life. Therefore the understanding of covalent bonding, including a simple mathematical model of first and second powers, has significant value in general education and for a better understanding of many general problems.

GRAPHICAL ABSTRACT

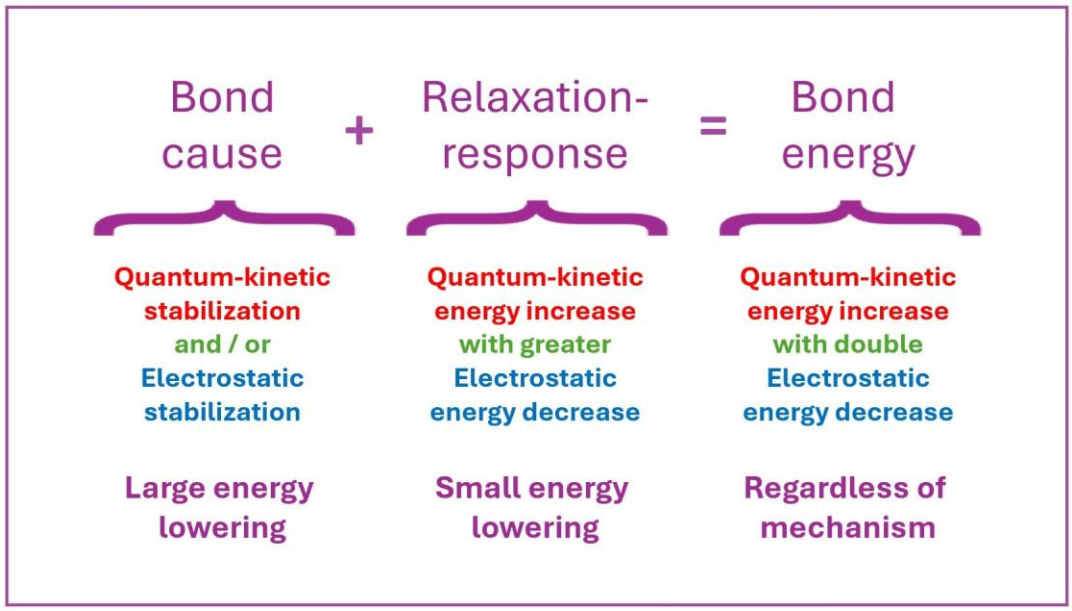
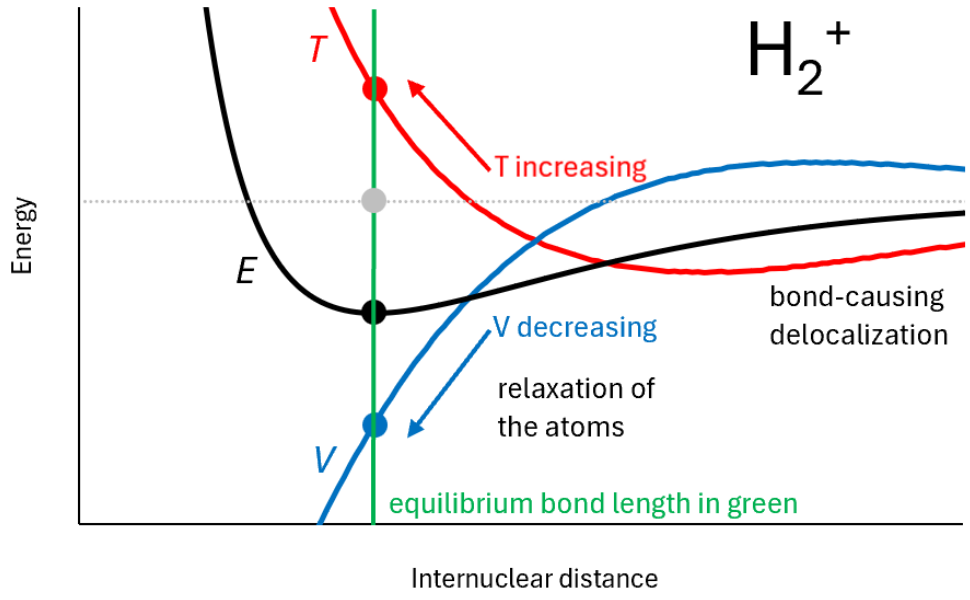


TABLE OF CONTENTS GRAPHIC



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OUTLINE

In the following “INTRODUCTION” we describe several important principles for the understanding of bonding, such as one-electron orbital-wavefunctions with a phase; local and delocal descriptions of molecular bonding; the difference of free and bound atoms.

The energetic view of bonding presents an apparent paradox when considering only the bond-causing perturbation, which is described in section “THE VIRIAL-THEOREM PARADOX”. Then we highlight “COVALENCY AS A QUANTUM PHENOMENON” before “SOLVING THE PARADOX” with the help of “A SIMPLE ELUCIDATING MODEL”, where we define an internal optimizing parameter of the molecule as a system of interacting and relaxing atoms, forming covalent, ionic and intermediate bonds. Any model needs an internal optimization parameter in order to allow the parts of the whole to relax to find their optimal state through the Variation Principle. In the case of chemical bonding, this relaxation leads to changes of the attractive and repulsive energy contributions an order of magnitude larger than the decisive total molecular energy, which shows that bond-explanations in terms of nuclear electron attraction or of electronic kinetic energy alone are useless.

The balance between kinetic and potential energy required by the virial theorem is discussed in relation to “EQUILIBRATION AND LE CHATELIER’S PRINCIPLE” and extended in “THE WIDESPREAD NEED FOR OPTIMISATION” which illustrates how many apparent paradoxes can be understood in a similar way.

In the "CONCLUSION" section, we emphasize that different causes within a coupled system can lead to different reactions that, in turn, result in similar outcomes. This illustrates that focusing solely on the outcome hinders an understanding of the phenomenon.

INTRODUCTION

Bonding is a central concept in chemistry whose character has long been believed to be electrostatic, especially by philosophers and educators and their students (Sanderson 1961, Jaffè 1963). The chemical bond can be defined as the physical origin holding molecular fragments together, which is the original empirical topological aspect of bonding at both the macro- and microscopic levels. The chemical bonding entails energy lowering that is much larger than common thermal energies of

the order of magnitude of RT. A significant energy lowering is the later developed physical causative aspect, also at both the macro-thermodynamic ΔG and the molecular micro-energetic ΔE levels.

The phenomenon of chemical bonding of elementary substances in materials, or of elementary particles in small or macro-molecules, can be viewed from various perspectives. At the one extreme, one considers only the result: the substance in the bottle obtained from chemical synthesis, and the electron density output for a crystalline sample of that substance by some commercial equipment with its software. This is the density oriented part of the quantum-crystallographic approaches (Grabowsky et al. 2017, Addiego et al. 2023, Krawczuk and Genoni 2024), where the bonding analysis heavily relies on Bader's so-called quantum theory of atoms in molecules (Bader 1990), where one should employ the density only. At the other extreme, we have the bonding of an isolated molecule in vacuum caused by interactions between fragments in chosen excited or 'promoted' states (Reed et al. 1988, Levine and Head-Gordon 2020). The middle position refers to structural units (molecules, unit-cells) with reference to most similar fragments in their ground states (Del Angel Cruz et al. 2025).

Orbitals and Densities. It is rather common to state that electron densities are observable and wavefunctions are not. Several caveats are appropriate here.

(**1**) Both electron density and wavefunctions (one-electron and many-electron) are not straightforwardly observable in the sense that the weight or temperature of a material specimen is observable. This is despite the fact that there are commercially-available equipment packages purporting to provide 'observed' electron densities.

(**2**) 'Observed' electron densities are *theoretically reconstructed* from scattering data (x-rays, electron beams) with the help of computed (atomic) electron densities that are part of a complicated process requiring many assumptions and ample experience in the field.

(**3**) Electron orbitals can only be observed, if defined through a specific physical one-electron process, and never from commercially-available equipment packages. Further, 'orbitals' are not generally uniquely defined; and there are many 'orbitals' for different purposes of discussion.[1] The many-

[1] Concerning the 'orbitals' of quantum chemistry: there are many different versions of the Hartree-Fock or Kohn-Sham model type that one may choose as: canonical, localized, natural (the latter in the case

electron wavefunctions in multi-dimensional phase-space can, at best, be computed. And it should also be remembered that theoretically reconstructing one-electron functions with ample experience from adapted observations is MUCH more complicated for one-electron wavefunctions than for one-electron densities.

(**4**) There are limited cases where one-electron orbitals have been 'observed' for specific physically well-defined processes, such as Dyson orbitals for one-electron ionization[2] or the natural excitation orbitals for simple one-electron excitations. In those cases the 'observation' of these one-electron orbitals is possible at a reasonably accurate level, but with much higher requirements regarding laboratory equipment, computing power, and the expertise of the staff. There are some tens of 'measured' and published orbitals in the literature, such as Rydberg orbitals of excited alkali atoms for time-independent and time-dependent cases (Weinacht et al. 1998, 1999), the highest occupied σ-lone-pair orbital of the N_2 molecule (Itatani et al. 2004), the a_1 and t_2 valence ionization orbitals of CH_4 in momentum space (Brion et al. 2001) and many other small molecules, and so on (Schwarz 2006).

Chemical Bonds. The covalent bond is often first presented at (high- or secondary-) school level as the Lewis (1916) picture of a shared pair of stationary (non-moving) electrons between two atoms. The bonding mechanism is presented in a classical electrostatic context, with the most important interaction being the shared pair of electrons between two nuclei 'gluing' them together through the attractive nuclear-electron Coulomb force. After atomic orbitals are first met, covalent bonds are rationalized as the molecular orbitals resulting from the overlap and quantum-interference of two atomic orbitals, the electrostatic mechanism of the bonding interaction remaining the same. Remarkably, the trivial consequence of potential energy rise by the transfer of charge from regions of highest density and lowest potential near the nuclei to the bond center, in many cases with higher electrostatic potential, is usually suppressed. At undergraduate level, the approximation of linear

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of a several-determinant approximation), orthogonal or non-orthogonal, and so on. The many graphical 'orbitals' in educational chemistry may be imprecisely 'defined' as "artists' impressions".

[2] If the ground state of an N-electron molecule can be reasonably well modeled in the one-electron orbital single-determinant approximation (by an N-orbital Slater determinant $\Psi(r_1,r_2,\ldots,r_N)$), and the same holds of the singly ionized cationic state $\Psi^+(r_2,\ldots,r_N)$, and the Dyson orbital $\varphi(r) = \int dr_2 \cdot \ldots \cdot dr_N \cdot \Psi(r,r_2,\ldots,r_N) \cdot \Psi^+(r_2,\ldots,r_N)$ has a norm only a little smaller than 1, just then this ionization orbital is physically well-defined and makes sense in the one-electron model, and it can be reconstructed from measurement, in a few specialized laboratories.

combinations of atomic orbitals (LCAO) is used to approximate the molecular orbitals (MOs) of covalent bonds (and non-bonds and anti-bonds). In particular, it is approximately assumed that the molecular orbitals are localized on two centers. More advanced classes extend this approach using Hückel theory for π systems (Hückel 1931), extended to all systems of orbital types by Hoffmann (1963) and, more generally, employ group theory to generate symmetry-adapted linear combinations of atomic orbitals also binding more than two atoms.[3]

Usually it is not mentioned that the two orbital approaches differ by the chosen "gauge" or "representation", that is by using either the *localized* representation of the MOs (LMOs) which offers a particularly simple description of single- and double-center reactions and electron lone-pairs. Or the so-called *canonical* representation of the MOs (CMOs, mathematically defined by a diagonal matrix of Lagrangian multipliers in the Self-Consistent Field equations; they are delocal), which offers a particularly simple description of UV-Vis spectroscopy, ionization processes and cyclic reactions (e.g. explained by the Woodward-Hoffmann rules).

Atomic Relaxation. Both explanatory, mathematically equivalent, models applying either localized or delocalized orbitals still involve generating coefficients for a linear expansion in atomic orbitals without modifying the atomic orbital functions themselves. In contrast, for many decades, most reliable computational molecular and solid-state approaches apply the linear expansion in empirically optimized sets of atom-localized *basis* orbital-functions, allowing for adapted atomic orbitals in molecules. As we shall see, in the molecular context, the *atomic* orbital wavefunctions change significantly when they relax in the molecule following the bond-causing perturbation. In addition the dominant electron configuration of free atoms is typically different from those atoms when bound (e.g. approximately $2s^1 2p^3$ for bound carbon instead of $2s^2 2p^2$, or $3d^g 4s^0$ in polar bound 1st row transition elements instead of free-atomic textbook $3d^{g-2} 4s^2$).

[3] Starting from conventional effective-one-electron-orbital single-Slater-determinant Hartree-Fock or Kohn-Sham self-consistent-field 'canonical' orbitals, some programs offer the possibility to localize the occupied MOs. This is achieved by a unitary transformation, leading to Lewis 2-center bonds for most sigma and pi orbitals and multi-center bonds for conjugated pi systems. We emphasize that when textbooks state that sigma bonds are 2-centric, they should say that they are *chosen* to be 2-centric. 6-centric pi orbitals on benzene, by contrast, are a natural result of the canonical, delocal calculation, with no attempt to localize the orbitals.

Ionic bonding is initially presented too as a straightforwardly electrostatic phenomenon in terms of the ionic charges. More sophisticated approaches consider the polarization of anions and the donation of their lone pairs into the empty valence shell of the cations, leading to a significant admixture of covalency as a correction, though this covalency is also, as we have mentioned, often considered an electrostatic interaction. (Further, the quantum mechanical Pauli repulsion between overlapping closed shells must be included to rationalize the equilibrium distances.)

The Energetic Aspect. The appealingly simple semi-classical electrostatic model has been considered by many as consistent with the virial theorem, given the greater magnitude of the total Coulombic potential bond energy, V, of the electrons and nuclei in the stable molecule, compared to electronic kinetic bond energy, T, in the expression

$$-V = 2T = -2E, \qquad (1)$$

where $E = T + V$ is the total energy of the bonded molecule. (Subtracting a similar equation for the non-bonded atoms or fragments, one obtains a similar equation for the bond energy.) This electrostatic view was held in the 1930s by Slater (1933) and Feynman (1939) and perpetuated by Coulson (1961) and, later, by Bader (2011). The electrostatic picture was also the subject of regularly appearing pedagogical articles (Venkataraman 2017, Joki and Aksela 2018, Zohar and Levy 2019, Brown 2020).

Misunderstandings by educators may also reinforce the view that electronic kinetic energy is of secondary importance. One of us (WHES) recalls several chemistry teachers asserting that electronic kinetic energies in molecules are basically classical thermal energies like most of the nuclear kinetic energies, and therefore more than an order of magnitude smaller than electronic and nuclear potential energies.

Lewis dot-and-cross bonding pictures convey the impression of static electrons and the term 'stationary states' generated by the Schrödinger equation may also mislead some to envisage stationary electrons. 'Stationary' however means for the Schrödinger equation that the electronic quantum distribution does not vary in time: the electrons keep the same averages and scattering of velocities, v, and of positions, x, i.e. Heisenberg's Δv and Δx 'uncertainties', in the stationary stable molecule. Significantly, Earnshaw's theorem (Earnshaw 1842) shows that in classical systems multiple

particles interacting via an inverse-square force law (gravitational or electrostatic) have to be in motion in order for a stable dynamical energy state to be established (such as in planetary systems).

Bonding, Energy and Overlap. Before we examine the chemical bond in detail, we should make clear that the formation of a chemical bond in real space-time is a complex process that requires a third partner, e.g., a solid surface, which catalyzes the atomic rearrangement and absorbs the released bond energy. In contrast, we here analyze bond formation as the conceptual difference between the separated atoms and the relaxed molecule in its semi-classical ground-state (meaning fixed nuclei of a semi-rigid structure; we do not consider the common large-amplitude nuclear motions in fluxional molecules of chemistry and biology). Our present discussion only aims at the explanation of the origin and magnitude of the 'bond energy'. The deduction of 'chemical bonding' from physics requires, in addition, the discussion of the real chemical process of bond formation, which is usually completely neglected in respective philosophical discussions.

We wish to ground our understanding of the chemical bond energy in the simplest physics that is acceptable at a semi-quantitative level: we treat the heavy, slow and semi-localized nuclei classically, and so they are in thermal equilibrium. Their surrounding electrons, by contrast, must be treated quantum mechanically. Due to their small mass and the quantization and the Pauli principle, their zero-point energies are already about two orders of magnitude or more higher than thermal energies and so we do not consider electronic energy exchange at thermal equilibrium in molecules. Instead, their internal energy is minimized as far as possible according to the quantum constraints of the system, with almost complete occupation of the electronic ground state. (Only metallic conductors possess a nearly continuous band of single-electron energy levels, allowing the uppermost electrons to be slightly thermally excited.)

We will consider the effect of the overlap of atomic orbitals of two atoms, forming a bond by achieving a lower-energy bonded state. As we will show later, the bond-causing mechanism is accompanied by a pronounced relaxation of the atoms bound in the molecule. Further, while most single covalent bonds are pair-bonds, one should not forget that the covalent bond is an inherently single-electron phenomenon, made clear by the qualitative similarity between the energy *vs.* bond length curves of H_2 and H_2^+ (see Supporting Information). Namely, if there is a low-energy single-

electron bonding orbital and two electrons are available, then two electrons will occupy this bonding orbital. The Pauli Exclusion Principle requires that the two respective spins are different, and that no more than two electrons occupy that (non-degenerate) spatial orbital. The one-particle overlap-bonding effect results in spin-pairing. Describing the resulting spin pairing as the origin of bonding, e.g. "The bonding comes from the spin-pairing arrangement of the atoms which yields a covalent bond" (Frenking and Knapp, 2007) inverts cause and result. Also note that dative and one-electron bonds do not involve the spin(s). But there always occurs interelectronic Coulomb repulsion when two electrons pair. For example, if each shared electron contributes binding energy on the typical order of 200 kJ/mol or similar and two electrons in the respective pair bond repel each other by 100 kJ/mol, the pair bond energy is still around 300 kJ/mol.

THE VIRIAL-THEOREM PARADOX

A quantum mechanical model commonly used to justify the molecular stabilization by a chemical bond resulting from the overlap of atomic orbitals – especially the energetic driving-force for extending the length of conjugated π systems – is the 'particle in a box' model (Atkins and Friedman 2010). This model shows that there is a decrease in the kinetic energy associated with the lowest single particle state wavefunction (and any individual higher energy state) as the 'box' length increases, since the curvature of the wavefunction (i.e. the second derivative of the wavefunction from the kinetic energy operator) decreases. It is often assumed that the electronic kinetic energy-density reduction in the overlap region of covalently binding atoms, accompanied by the delocalization of the valence electrons originally localized at the atoms, implies that the total electronic kinetic energy of the stable molecule in equilibrium is reduced too. But this is not permitted by the general laws of mechanics, and the virial theorem for Coulomb forces tells us that a *relaxed* molecule in equilibrium has a lowered total energy of minus an increased kinetic energy.

The virial theorem[4] holds for conservative dynamical systems. In the case of an inverse-square force law – first applied to gravitational problems but equally applicable to electric forces – the

[4] The virial theorem, more generally, is: $2T = -r\,dV/dr$, classically for the values, and quantum-mechanically for the integrals over the operators times wave functions (for classical nuclei and

potential energy, V, and kinetic energy, T, must satisfy for a system in equilibrium, i.e. with all forces balanced,

$$2T = -V \tag{2}$$

This result is a general feature of inverse-square force laws in conservative systems at equilibrium, regardless of whether the system is being treated classically or quantum mechanically. In fact, the $-V = 2T$ expression of the virial theorem is a special case of a more general virial theorem for point particles in a diatomic state with internuclear distance R:

$$T_e(R) = -E(R) - R \cdot \partial E / \partial R \tag{3}$$

$$V(R) = +2E(R) + R \cdot \partial E / \partial R \,, \tag{4}$$

where T_e is the electrons' kinetic energy and $\partial E/\partial R$ represents an unbalanced force between the atoms in the molecule at R (Schwarz et al. 2025).

It is easiest (albeit simplistic) to appreciate the validity of the virial theorem for a classical hydrogen atom[5] if we imagine the electron with mass m and speed v in a circular orbit of radius r in which the centrifugal force, mv^2/r, is balanced by its coulombic force of attraction to the nucleus, $Ze^2/(4\pi\varepsilon_0 r^2)$, where ε_0 is the permittivity of free space, Z is the proton number (for hydrogen, $Z = 1$) and e is the fundamental electric charge. Equating the two force expressions gives $v^2 = Ze^2/(4\pi\varepsilon_0 mr)$. Substituting this result into $T = \frac{1}{2}mv^2$ gives $T = Ze^2/(8\pi\varepsilon_0 r) = -\frac{1}{2}V$. As we shall see, it will also be possible to show the validity of the virial theorem easily in a quantum and molecular context.

While it is widely appreciated that the virial theorem holds for the hydrogen atom, it is seldom discussed in an educational context for molecules. This may, in part, be because $-V = 2T$ only holds at stationary points on the reaction path, i.e. at the energy minimum of the molecule, at the dissociated

quantum electrons). $-dV/dr = F$ is the force; for potentials $V(r)$ varying as a power of r, r^n: $r\,dV/dr = n\,V$; then $2T = n\,V$. For the Coulomb potential, $n = -1$, and that gives the 'common' form of the virial theorem, $2T = -V$. For a box, the potential inside is constant, r^0, and can be chosen freely, but there are jumps of V at $r = 0$ and $r =$ Length; hence the form of the virial theorem for the box is involved.

[5] Despite this obviously flawed model of a circular orbit having angular momentum in its ground state, it should not be forgotten that Bohr's semiclassical approach with this model predicted the spectral series of H, He^+ and D with extremely high numerical accuracy; while it failed for the simplest molecule, H_2^+, which triggered the search for a better model, quantum mechanics.

fragments at infinite separation, and at the energy saddle points of reaction transition states (other geometries require the $R{\cdot}\partial E/\partial R$ force term, see above).

Although it is typically called the virial 'theorem', it is a lemma rather than a fundamental law of nature. In the context of this paper it is used as a diagnostic tool to test the validity of approximate molecular wavefunctions. If the virial theorem holds, it doesn't necessarily prove the wavefunction is correct, but if it does not hold, the proposed wavefunction is certainly inaccurate.

COVALENCY AS A QUANTUM PHENOMENON

The covalent bond is a fundamentally quantum mechanical phenomenon, which was stressed in the famous Heitler and London (1927) paper. This is apparent from the initial overlap of atomic orbitals, which depends on the relative phases of the overlapping orbitals (with large bonding and antibonding effects arising from in-phase and anti-phase interactions, respectively), an intrinsically quantum property of the electron wave that does not show up for the classical phase-less charge density distribution. Indeed the overlap of atomic orbitals from different atoms is the quantum-mechanical interpretation of the Lewis shared-pair bond. While this constructive-overlap bonding interaction can occur for a single electron, a second electron with opposite spin can also occupy this one-particle state (with opposite spin according to the Pauli principle); while this introduces Coulomb repulsion between the two electrons in the same spatial region, the quantum-mechanical bonding energy lowering is often large enough to overcompensate. This overlap causes an increased interatomic electron delocalization that is described with the particle-in-a-box model that illustrates the increased lowering of the kinetic energy of the ground and excited state wavefunctions for increased expansion of the box. We stress here that spin-pairing is one of the *results* of the formation of a bonding orbital, it is not the *cause* of covalent bonding.

The sum of *two* overlapping or non-overlapping atomic orbitals gives a 'delocal' *two*-center molecular orbital; that reduces the kinetic energy density if and only if the molecular wavefunction is less curved and flatter than the two atomic orbitals: that happens when the two orbitals significantly overlap with negative slope of the left orbital and positive slope of the right orbital cancelling each

other, giving a flat molecular orbital in the middle. A famous article by Goddard and Wilson (1972) called it “contra-gradience”, the origin of covalent bonding.

The importance of the kinetic energy in bonding was first recognized by Hellmann (1933). He described the quantum-mechanical energy stabilization of molecules as a reduction in kinetic energy through electron delocalization, albeit only qualitatively. An independent, theoretically rigorous analysis was initiated by Ruedenberg (1962), who carefully analyzed all terms in the quantum mechanical energy expression, also in consideration of the quantum mechanical Variation Principle. He demonstrated the fallacy of all arguments in support of the electrostatic origin of covalency and showed that bonds are formed through the kinetic energy lowering by interferences of orbitals from those atoms between which the bonding electrons are individually shared. In particular, all early efforts of estimating the binding energy of H_2^+ and H_2 had replaced the atomic kinetic energy terms by $T_a = (E_a - V_a)$, which resulted in a molecular energy expression that was dominated by Coulomb terms, reinforcing the false assumption of covalency as a Coulomb effect. Another persistent misconception is the assumption that covalency is based on charge accumulation at the bond center. However, bonds do exist without a charge accumulation or without a strong attraction potential at the center. Many different reorganizations of the molecular electronic charge distribution can reduce the total potential energy (Schwarz and Mons 1989). Moreover, the charge accumulation is sometimes ‘created’ by the author by a clever selection of reference ions, or of the individual orbitals of open-shell atoms,[6] as pointed out frequently (Schwarz et al. 1986, 1989a,b, 1992, Mensching et al. 1989, Wang et al. 1991, Irle et al. 1992).

Ruedenberg also resolved the above-mentioned virial theorem paradox. The work was extended and deepened together with his co-workers from 1962 onwards (Feinberg et al. 1970, Feinberg and Ruedenberg 1971, Ruedenberg 1975, Bitter et al. 2007, 2010, Ruedenberg and Schmidt 2007, 2009, Schmidt et al. 2014a,b, Bacskay et al. 2018), and by other researchers (Baird 1986, Nordholm 1988,

[6] The idea of charge accumulation is most problematic with open p subshells as there is no unique reference state given by Nature. For instance, in the case of F_2, it was found, experimentally and theoretically, that there is a slight density reduction at the bond center with reference to spherical F $p_x^{5/3}p_y^{5/3}p_z^{5/3}$ (the common choice in quantum crystallography), and therefore Bader’s QTAIM ‘predicts’ no bond in F_2, whereas a slight ‘bond density’ is obtained with reference to F-$2p_{\pi x}^2 p_{\pi y}^2 2p_{\sigma z}^1$.

Bacskay et al. 1997, Rioux 1997, Carlton, Rioux, DeKock (separately) 1999, Gordon and Jensen 2020, Nordholm and Bacskay 2020, Schwarz et al. 2025). In the variation approach, the radial and angular shapes of the free atomic orbitals are improved for the bonded atoms in the molecule by a computationally straightforward but laborious technique.

Concerning the atomic relaxation in the special case of the H atom without any restrictions of orthogonality on occupied atomic core shells, and without any higher angular-momenta orbitals in the valence shell, one can do an efficient variation even by hand calculation, by simply varying the exponent of the atomic orbital, thereby minimizing the total energy of the bonded system. This was first achieved by Finkelstein and Horowitz (1928). This energy minimization makes the exponent larger in magnitude than in the free atomic orbitals, causing the orbital to contract towards the nucleus. The physical origin is the drive to the energy minimum by the electron getting closer to the nucleus and the result is the contraction of electron density, represented by a larger factor before the r in the wavefunction's negative exponent. The energy minimization also shortens the bond length from its pre-minimization length: the contracted atoms, being smaller, come closer together at equilibrium.

The orbital contraction increases the magnitude of the potential energy[7] such that in the total-energy-minimized state the virial condition, $-V = 2T$, is met. This serves as a confirmation of the validity of the approach – indeed the necessity of the energy-minimization process that optimizes the wavefunction – and the failure of the unmodified wavefunction (i.e. the linear combination of free-atom orbitals) to describe the molecular equilibrium state and satisfy the virial theorem. As well as delocalization and orbital contraction, the cited studies also describe polarization as part of the process, which leads to the deformation of orbitals of similar energy, corresponding to s-p or s-p-d mixing, i.e. hybridization. However, this is acknowledged as a small effect in the special case of hydrogen atoms, where the valence shell has only a single 1s orbital, and will not be considered further here.

[7] The potential energy consists of 3 terms: nucleus-nucleus repulsion, electron-electron repulsion, and electron attraction by two nuclei. To the lowest level of approximation the relative sizes of these 3 energies are of order +1, +1, –2, respectively, cancelling each other largely. The correct values deviate somewhat from these ratios and give a small negative sum. Note that the huge absolute values of these 3 terms give little insight and understanding (see Schwarz et al. 2025).

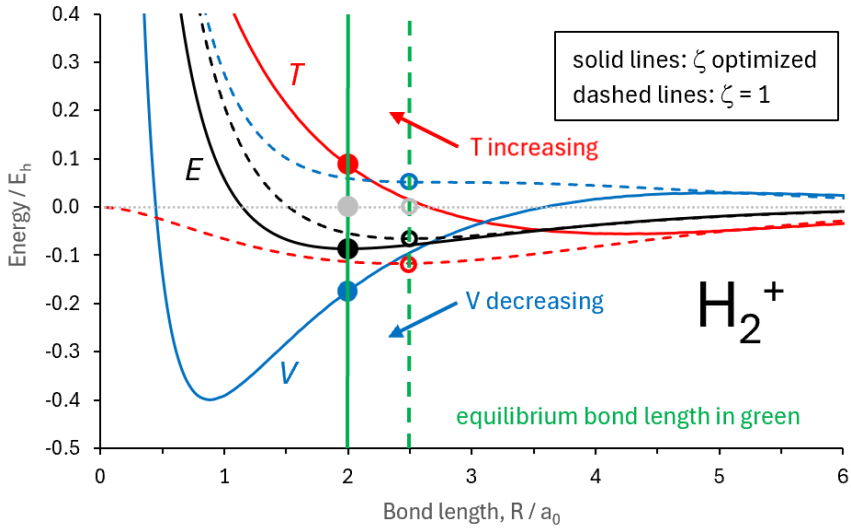


Figure 1. Energy of the H_2^+ molecular ion (valence bonded; in Hartrees; 1 Ha ≈ 2626 kJ/mol) against internuclear distance, *R* (in Bohr radii; 1 a_0 ≈ 52.9 pm). Energy differences relative to H (and H^+), are based on calculations by one of us (CSM) that closely resemble data for H_2^+ generated by Nordholm and Bacskay (2020), which is also qualitatively similar in appearance to their data for H_2 (see Supporting Information). The dotted lines were calculated using the unmodified atomic orbital exponents of the 'frozen free atoms'; the solid lines were calculated with an optimization of atomic orbital exponents for the 'H atoms in the molecule'. Color code: red for kinetic energy, blue for potential energy, black for total energy. The vertical solid green line and colored solid dots indicate the optimized internuclear equilibrium distance, R_0 (exp. 1.99 a_o ≈ 105 pm), at the total molecular energy minimum with virial relation $-E_0 = -\frac{1}{2}V_0 = +T_0$ (holding for the ζ-optimized wavefunction). The two diagonal arrows illustrate the kinetic and potential energy changes due to the deformation response of the atoms bonded in the molecule.

The numerical values of the energy vs. internuclear distance curves shown in Figure 1 closely resemble those generated by Nordholm and Bacskay (2020) for H_2^+, which are similar in appearance to their graph for H_2 (see Supporting Information). The dotted lines show the internal potential (*V*) and kinetic (*T*) and the total (*E*) energy of the H_2^+ molecular ion with the nuclei artificially fixed at different distances, *R*, when the atomic orbital exponents were not varied. Below about 4 Bohr radii (nearly twice the bond length), the improved energy components *T* and *V* of *E* (bold curves, obtained with optimized exponents for the atomic orbitals in the molecule) begin to deviate strongly from the values of the model of unmodified free atoms in the molecule (dashed curves) while the total energy sum, *E*, is still approximated acceptably. We see that at large internuclear distances (≥ 5 Bohr radii) the minimized energies are well reproduced by the simple approximate non-optimized atomic orbital model. At shorter internuclear distances, as the equilibrium bond distance is approached, we see the *V* and *T* curves strongly deviate from the simple model curves in opposite directions and even cross

each other until the –V = 2T condition is established at the total-energy minimum at internuclear distance R_0. It is only at the energy-minimized state that the $-V = 2T$ condition is satisfied, as would be expected as this law only pertains to the equilibrium state. It is noteworthy that when there is no variation of the atomic orbital exponents, the potential energy is always positive, so anti-bonding, i.e. greater than the atomic non-bonded state, refuting the potential-energy electrostatic mechanism. This is because the increase in electron density around the bond center means there is less electron density where it was mainly before, i.e. closer to each nucleus where the potential energy is much lower than between the two nuclei!

SOLVING THE PARADOX

Feinberg and Ruedenberg (1971) discussed the paradox of kinetic energy in covalent bonding: while the bonding mechanism lowers kinetic energy density in the overlap region through electron delocalization, in the equilibrium bonded state the electron kinetic energy value is greater than in the non-bonded atomic state (as confirmed in Figure 1).[8] The answer is to distinguish between the causing mechanism and the relaxation-response of the system, and between the electronic charge and energy density distributions in different regions of space and the observable total charge and energy values. Covalent bonding is dominantly driven by electron delocalization from orbital overlap – more precisely, a more extended and connected density distribution – and resulting kinetic-energy lowering: this mechanism acts as a perturbation on the atoms in the system. The perturbed state responds by relaxing, i.e. minimizing its energy just a little in comparison to the large lowering of the potential energy (blue arrow in Figure 1), by shifting electron density from the outer spatial regions towards the vicinity of the nuclei,[9] at the expense of increasing the kinetic energy by nearly the same amount (red

[8] Strictly, it is only the kinetic energy density summed over all space that is uniquely defined. The integrand in the integral may be changed in many ways, for example by partial integration, leading to different distributions over space, but with the same observable integral value. In practice, a physically realistic representation is chosen to yield rationally and intuitively correct and convincing arguments and explanations, or one that is easily integrated.

[9] We remind the reader that hydrogen is exceptional in having no core shells, where the Pauli Principle would require incoming electrons to take up significant momentum and kinetic energy, the so-called Pauli repulsion effect; therefore, in 'normal' atoms with occupied core shells, there is only a little density contracted towards the nucleus, but towards the inner valence shell, and this still contributes a significant amount of kinetic energy.

arrow in Figure 1). In the molecular bonded state the molecular orbital is more smooth and flat around the 'bond center' than the atomic orbitals, which (by decreasing the magnitude of the wavefunction's curvature and second derivative) lowers the kinetic energy quantum mechanically. This 'paradoxical' relaxation process is illustrated by the crossing over of the potential and kinetic energy curves in Figure 1 as the internuclear distance approaches the equilibrium value.

An important consequence of the relaxation-response, illustrated by this paradox, is that it obscures the mechanism that initiated the process. The hugely plus and minus modified resulting values of the potential and kinetic energies in the molecule in its equilibrium state therefore hold no information about the bonding-causing mechanism. This refutes the deduction that the larger magnitude of the potential energy means that bonding must be driven by an electrostatic mechanism.

A SIMPLE ELUCIDATING MODEL

Many systems in the real material and social worlds are quite stable over time due to the balance of opposing forces. For a simple model[10] we desire a single internal parameter to describe a relevant internal property of the system and its value that guarantees stable internal equilibrium of opposing forces inside the system. In the case of a molecule, the opposing 'forces' or 'pressures' on the equilibrium of the bonded time-stable state are connected with the kinetic and potential energies of the system of valence electrons. We then optimize this internal parameter in order to minimize the total energy as the sum of positive kinetic and overall-negative potential energies to guarantee a stable state.

The kinetic energy, T, is defined in terms of velocity, v, or momentum, $p = mv$: $T = mv^2/2 = p^2/2m$, where m is the mass of electrons that make up the bonding of the molecule in the field of the heavy nuclei and their inner occupied inert core shells, their center basically being at rest (except for zero-point and small thermal effects); the potential energy, V, is, in our model, defined in terms of the average distance of the electrons from the nuclei, r, and is proportional to $-Z_{eff}/r$, where Z_{eff} is the

[10] In real molecules more parameters will be required to describe the different bond angles and atomic radii, and the many individual electrons, but a single parameter can show the essence of the important characteristics of a molecule satisfying the virial theorem.

effective nuclear attracting charge of the valence electrons by the atomic cores in the molecule. We wish to relate electron momentum and its radial distance, which can be done through judicious use of Heisenberg's Uncertainty Principle (the foundational quantum principle), in addition to describing the reality by a spatial wave-field with phases, replacing the point-particle's coordinates.

(1) Defining the Internal Parameter. We start with the familiar form of the Uncertainty Principle for 1 dimension, $\Delta x \cdot \Delta p \geq \hbar/2$, where $\hbar$ is the reduced Planck constant, $h/2\pi$. Considering for simplicity our bonded system to be one-dimensional, we approximate r to be x. The factor ½ in the inequality holds for the case of a harmonic oscillator potential proportional to $+x^2$. For most other types of interactions, it is empirically found that $\Delta r \cdot \Delta p \approx 1\hbar$ for the ground state with assumed quantum number n=1, and $\Delta r \cdot \Delta p \approx n\,\hbar$ for the nth excited state. We now define our coordinate system to have its origin at the center of gravity of the whole molecule with internal motions in our one-dimensional picture, such that the whole molecule remains at rest at the origin. A symmetric molecule's electronic wavefunction will have a distribution symmetrically around the origin of r and p values. We will approximate the average magnitudes of these quantities to be the root-mean-square (r.m.s.) of their distributions; similarly we will approximate the inverse of these quantities to the inverse of the r.m.s. value. For the H_2 molecule, in atomic units, we therefore write $r \cdot p = 1$ (taking $\hbar$ as a unit).

With that simple relation between r and p, we can write the energy functions T and V in terms of either of these parameters, r or p. It is interesting to compare the effect of using each of these parameters.

(2) Using the Internal Molecular Parameter *p* (average electronic velocity × mass). Applying $r \cdot p = 1$, we deduce for the average valence electron that $T \propto +\frac{1}{2}p^2$ and $V \propto -p^1$ and apply the proportionality constants K and Z to the T and V functions, respectively:

$$T = +\tfrac{1}{2}K \cdot p^2 \qquad\qquad V = -Z \cdot p^1 \,. \tag{5}$$

We now minimize the total energy, $E = T + V$, with respect to the p parameter to find its optimized value, p_{opt}:

$$\frac{dE(p)}{dp} = K \cdot p_{opt} - Z = 0$$

$$\therefore p_{opt} = \frac{Z}{K}. \qquad (6)$$

We now substitute the optimized value for p back into the T and V functions to obtain the optimized energy values, T_{opt} and V_{opt}:

$$T_{opt} = +\frac{Z^2}{2K} \qquad (7)$$

$$V_{opt} = -\frac{Z^2}{K}. \qquad (8)$$

We see that $2T_{opt} = -V_{opt}$ and the virial diagnostic for our model case with an optimized p parameter is satisfied.

(3) Using The Internal Molecular *r* Parameter (average electronic distance from nuclei). Applying $r\,p = 1$, we deduce that $T \propto +\frac{1}{2}r^{-2}$ and $V \propto -r^{-1}$ and apply the same K and Z parameter values as before to the T and V functions, respectively:

$$T = +\tfrac{1}{2}K \cdot r^{-2} \qquad V = -Z \cdot r^{-1}. \qquad (9)$$

We now minimize the total energy, $E = T + V$, with respect to the r parameter to find its optimized value, r_{opt}:

$$\frac{dE(r)}{dr} = -K \cdot r_{opt}^{-3} + Z \cdot r_{opt}^{-2} = 0$$

$$\therefore r_{opt} = \frac{K}{Z}. \qquad (10)$$

We note that $p_{opt} \cdot r_{opt} = 1$ (Heisenberg Uncertainty Principle) and now substitute the optimized value for r back into the T and V functions to obtain the optimized energy values, T_{opt} and V_{opt}:

$$T_{opt} = +\frac{Z^2}{2K} \qquad (11)$$

$$V_{opt} = -\frac{Z^2}{K}. \qquad (12)$$

We see that we have deduced the same values for T_{opt} and V_{opt} that we obtained from the p parameter and that, of course, the virial diagnostic is satisfied again.

(4) Ionic and Covalent Bonding. With ionic bonding being essentially electrostatic, the bond-causing mechanism mainly affects the potential energy due to the interaction between A^+ and X^- ions

following the formal charge transfer of an electron from a weakly (A) to a strongly (X) electronegative atom. With the covalent bond-causing mechanism being orbital overlap, leading to a more diffuse / delocalized wavefunction, it mainly affects the kinetic energy in the spatial region of atomic orbital overlap (as discussed earlier). We can therefore model these two different main bonding mechanisms through modification of the coefficients, respectively, in the V and T expressions. We say there is a reduction by a factor of κ in the K constant from covalent bonding (due to lowering the kinetic energy density in the overlap region) and an increase by a factor of ζ in the Z constant (which lowers the potential energy) from ionic bonding. In terms of the r variable, the functional relations are:

$$T_{bonding} = +\frac{K(1-\kappa)}{2r^2} \tag{13}$$

$$V_{bonding} = -\frac{Z(1+\zeta)}{r}. \tag{14}$$

So κ and ζ are both defined to be positive for energy lowering and bonding in these equations. They also modify the optimized r value, $r_{opt} = \frac{K}{Z}$. If only the kinetic energy is lowered (by the bond-causing mechanism for covalency) and then r is optimized, the result is $r_{opt} = \frac{K(1-\kappa)}{Z}$; if only the potential energy is lowered (by the bond-causing mechanism for ionic bonding) and then r is optimized, the result is $r_{opt} = \frac{K}{Z(1+\zeta)}$. Note that both mechanisms describe a reduction in the optimized radial nuclear-electronic distance, consisted with observed differences between sums of atomic radii and bond lengths. Further, the atoms bound in covalent molecules or ionic crystals are on the average smaller in size than the separated free atoms in free space.

(5) Covalent Bond Energies. We apply just the $r_{opt} = \frac{K(1-\kappa)}{Z}$ from the kinetic-energy-lowering bond-causing mechanism. Substituting this into the $T_{lowered}$ function expression gives the optimized kinetic energy number value,

$$T_{opt} = +\frac{Z^2}{2K(1-\kappa)}. \tag{15}$$

We note that the optimization process has *increased* the kinetic energy value from the non-bonded value, $\frac{Z^2}{2K}$, following the covalent bond-causing mechanism of *decreasing* the kinetic energy function.

The optimization of the potential energy value accordingly becomes

$$V_{opt} = -\frac{Z^2}{K(1-\kappa)}, \tag{16}$$

showing that the potential energy value (unlike the kinetic energy value) has been lowered in the equilibrium covalently bonded state. It is evident that $2T_{opt} = -V_{opt}$ and the virial diagnostic is satisfied.

(6) Ionic bond energies. We apply just the $r_{opt} = \frac{K}{Z(1+\zeta)}$ from the potential-energy-lowering mechanism. The optimization of the kinetic energy value accordingly becomes

$$T_{opt} = +\frac{Z^2(1+\zeta)^2}{2K}. \tag{17}$$

Again, we see that the optimization process has increased the kinetic energy value compared to its non-bonded value, $\frac{Z^2}{2K}$, following the ionic-bond-causing mechanism which, to the lowest order of approximation, does not influence the kinetic energy function.

The optimization of the potential energy value accordingly becomes

$$V_{opt} = -\frac{Z^2(1+\zeta)^2}{K}, \tag{18}$$

showing that the potential energy value (again, unlike the kinetic energy) has been lowered in the equilibrium ionically bonded state. It is clear by inspection that these ionic T_{opt} and V_{opt} values also satisfy the virial diagnostic. These results are reproduced if the process is repeated using p as the internal parameter that is optimized.

(7) Intermediate Bonding. Chemical bonds are typically regarded as intermediate between ionic and covalent in most cases. However, our model shows that regardless of the bond-causing mechanism, once the system has equilibrated, i.e. internal parameters optimized and total energy minimized, the resulting T value is raised from the atomic value and the V value and total energy, E, lowered in accordance with the virial theorem. Moreover, these optimized energy values, i.e. the observable energies of the stable compounds, shed no light on the bond-causing mechanism. So nothing can be said about any intermediate bonding either from these optimized and observed or observable energy values.

In the context of intermediate bonding, it is worth mentioning metallic bonding, since it is on an equal footing with ionic and covalent bonding in the van Arkel triangle of bonding (Leach 2026).

Further, between the extremes of the localized two-center-two-electron bond and the delocalized metallic bond, there are molecules with covalent bonding delocalized over three or more atoms, such as the aromatic or 'resonating' ones.

The interpretation of metallic bonding in the optimization / virial picture is to apply the overlap-and-delocalization bond-causing mechanism. In the simplest approach, for the unbonded state, we equate the first ionization energy of the free atom, ≈7±3 eV, to $T = -\frac{1}{2}V = -E$ of the highest energy electron. Application of the bond-causing mechanism lowers the kinetic energy density: the electrons located in the valence shells of the isolated atoms are delocalized uniformly over the metallic solid, like an electron gas. The associated relaxation somewhat contracts the smooth electron density around the atomic cores, lowering the potential energy and raising the kinetic energy in accordance with the virial theorem. In the equilibrium bonded state, $T = -\frac{1}{2}V = -E \approx 12$ eV such that the metallic bond energy is ≈5±4 eV, with the typical metallic binding energy per atom being ≈3±2 eV. This simple representation illustrates how metallic bonding is a generalization of covalent bonding in this optimization / virial picture. Its shortcoming is that it only considers the highest energy electrons, whereas the macroscopic cohesion energy of the metallic phase refers to the mean average of the whole electronic energy level band. Indeed the metallic conduction electrons are at the top of the metallic valence bands, while some strongly covalent binding and more localized electrons are at lower energies. It is noteworthy that the weak metallic bonding of the soft alkali metals is consistent with the particularly diffuse s valence electron in the atomic state (radius of the K 4s ≈ 2¾ Å): the delocalization of this s valence electron in the metallic phase is less of a perturbation than the delocalization of less diffuse d electrons in d-block elements (radius of the Cr 4s ≈ 2 Å, Cr-3d ≈ ¾ Å).

In the general case where there are both covalent and ionic contributions to the bond-causing mechanism, the earlier expressions for the optimized energy values before and after bond formation can be generalized as:

$$T_{opt}^{bonded} = T_{opt}^{atomic} \frac{(1+\zeta)^2}{1-\kappa} \tag{19}$$

$$V_{opt}^{bonded} = V_{opt}^{atomic} \frac{(1+\zeta)^2}{1-\kappa} \tag{20}$$

$$E_{opt}^{bonded} = E_{opt}^{atomic} \frac{(1+\zeta)^2}{1-\kappa}. \quad (21)$$

To the lowest order of approximation the energy changes on bonding are therefore:

$$\Delta T_{opt} \approx (\kappa + 2\zeta) T_{opt}^{atomic} \quad (22)$$

$$\Delta V_{opt} \approx (\kappa + 2\zeta) V_{opt}^{atomic} \quad (23)$$

$$\Delta E_{opt} \approx (\kappa + 2\zeta) E_{opt}^{atomic} . \quad (24)$$

Bearing in mind that p and r are inversely proportional, it furthermore follows that:

$$\Delta p_{opt} \approx +(\kappa + \zeta) p_{opt}^{atomic} \quad (25)$$

$$\Delta r_{opt} \approx -(\kappa + \zeta) r_{opt}^{atomic} . \quad (26)$$

EQUILIBRATION AND LE CHATELIER'S PRINCIPLE

The perturbation to the kinetic and/or potential energy due to the bond-causing mechanism(s) followed by the system's relaxation-response to establish an internal equilibrium and energy minimization has a passing resemblance to the action of Le Chatelier's principle on a chemical dynamic equilibrium that is subject to an external change. We stress that, while thermodynamic theory works exactly, Le Chatelier's principle is not a basic law but a corollary that only applies to carefully chosen variables in a suitable context (Münster 1970). Therefore the reader should not be surprised if the naïve application of Le Chatelier's 'principle' sometimes does not work as expected. We believe it makes for an interesting comparison as we see different types of behavior.

- The covalent bond-causing mechanism introduces the perturbation of lowering the kinetic energy function by a factor of (1–κ) due to orbital overlap. However, the system's relaxation-response leaves the kinetic energy value higher than it was before the perturbation by a factor of ≈(1+κ). We call this behavior over-Le-Chatelier as the 'dynamic equilibrium' of kinetic and potential energy has opposed the perturbation to such an extent that kinetic energy becomes greater than it was originally.

- The ionic bond-causing mechanism introduces the perturbation of further lowering the (negative) potential energy function through the Coulomb interaction between opposite charged ions by a factor of (1+ζ). However, the system's relaxation-response leaves the potential energy value even

lower than the perturbed value, by a factor of ≈(1+2ζ). We call this behavior anti-Le-Chatelier as, rather than oppose the perturbation, the dynamic equilibrium has added to it.

THE WIDESPREAD NEED FOR OPTIMIZATION

The variation process is an example of a perturbation and a subsequent relaxation-response, where the delocalization of wavefunction and electron density and the respective energy changes due to orbital overlap is the perturbation; and the change of wavefunction (for H mainly by variation of the radial orbital exponents), the contraction of the orbitals, the minimization of the total energy, and the satisfaction of the virial theorem are the relaxation-responses of the system. In more general cases, radial orbital optimization is more complex than simple radial scaling. The simple overall contraction of orbitals is only particularly energy-efficient for the uniquely simple hydrogen atoms, without core shells and with only a single valence orbital, but guarantees the fulfilment of the virial diagnosis. In atoms with core shells, account needs to be taken of Pauli repulsion[11] of contracted valence electrons by the core shells, but this can be “easily” achieved computationally by optimized mixing of several differently extended basis functions (so-called multi-zeta basis). Further, the general response of free atomic orbitals in bound compounds also comprises angular deformation, i.e. mixing of atomic orbitals of different angular momentum (s-p-d-f hybridization).

The need for an optimization (i.e. an energy minimization) of the system, rather than only applying a perturbation according to a proposed mechanism, is not surprising in the light of the virial theorem: a mechanism which changes the kinetic energy density in some spatial region of the system in isolation necessarily moves the system away from its internal equilibrium. Furthermore, the kinetic and potential energies have opposing effects on the electron density: increasing electron kinetic energy

[11] Pauli repulsion means the consequences of the Pauli Exclusion and Heisenberg Uncertainty Principles. When two independent fragments with filled electron shells are brought together, they usually respond by relaxation in (position-momentum) phase space, with an overall energy increase, often called steric repulsion. This “Pauli repulsion” is the physical cause of the fragment relaxation in the whole and approaches zero in its stationary state; i.e., trivially, there is “Pauli Repulsion” between the unrelaxed overlaid fragments (which is not a physical state in reality), that disappears in the physically relaxed observable state (Poater et al. 2006, Henrichsmeyer et al. 2025). Since the Bader community only allows observing the result of a process, but not asking for its physical cause, they argue that the Pauli repulsion is only in the eye of those ones who want to observe it (Bader 2006).

serves to expand the electron cloud; increasing the magnitude of the potential energy serves to contract the cloud towards regions where the potential energy function is low. Nature seeks a balance where these kinetic and potential energy 'pressures' are balanced so that all forces are balanced inside the molecular system, which is encapsulated in the virial $-V = 2T$ condition.

The need to optimize opposing factors, and the seeming paradoxes that can result, is widespread in nature and society, even. This is illustrated in the following examples.

- Recently electron-pair repulsion and rotational barriers in non-rigid molecules were rationalized using similar arguments based on an optimization of the molecular orbitals taking into account opposing effects (Schwarz et al. 2025).
- Feinberg and Ruedenberg (1971) made the comparison with an apparent paradox in piloting orbital space craft. A pilot in a satellite orbiting the Earth in a stable orbit wishes a shorter orbital period and therefore an orbit closer to the Earth, which implies a greater kinetic energy of the faster satellite. To achieve this acceleration, a retro-rocket is fired to decelerate the satellite momentarily. This leaves the kinetic centrifugal energy too low and, as they put it, "the centrifugal force is too weak to counteract the 'gravitational suction' of the earth." As a result, the absolute potential energy decreases as the satellite is drawn closer to the Earth, and the kinetic energy increases, conserving energy until satisfying the virial theorem in the lower orbit. So the 'mechanism' of the orbit change is decreasing the kinetic energy, but the final equilibrium state in the new orbit has a higher kinetic energy than the initial state, so that the higher centripetal force can balance the higher gravitational attraction at the lower shorter faster orbit. This runs very much in parallel to the 'paradox' of kinetic energy in covalent bond formation.
- In stellar physics there is the 'paradox' of the apparently negative heat capacity of stars in hydrostatic equilibrium. When a star in hydrostatic equilibrium radiates, one would expect that the temperature drops, decreasing the internal pressure according to the gas law; but this leads to the star's gas cloud contracting towards its center of gravity, thereby heating it up, like a hand pump for a bike (Prialnik 2000).
- Speed limits on roads can increase traffic flow (Bidoura Khondaker 2015).

- Tax rate reduction can increase the state's overall tax revenue: Laffer's law (Trabandt and Uhlig 2011).
- Global warming due to climate change may lead to cooling in some areas.
- At the level of politics and moral philosophy in society there is perhaps also a parallel with some actions leading to the opposite consequence of the hoped for and expected one: well-intentioned is not always well done.

CONCLUSION

Covalent bonding has a physical *origin*, which is first of all the constructive wave interference of overlapping, partially occupied atomic valence orbitals. This lowers the total energy by significant lowering the bond-parallel quantum kinetic energy component in the overlap region. It works best for significant overlap density. However, upon relaxation of the atoms in the molecule, there is a change of the molecular wavefunction that causes a smaller or larger total molecular energy improvement, and huge changes of potential and kinetic energies dominantly inside the atoms in opposite directions, as shown in Figure 1. The satisfaction of the virial theorem in this relaxation process confirms the validity of this approach.

The 'pedagogical' model and discussion (mathematically simple enough that it can hopefully be digested by some of the powerful and influential in philosophy and society) highlight the consequences of two opposing contributions, T and V, to the total electronic energy of the molecule that both change upon relaxation even when only one individual term with parameter, κ or ζ, is changed. The final, relaxed numerical values of the energy components of the system do not vary as the parameters (not even in the lowest order, as one might naively expect) as the parameters that describe the functional dependence of the components. This is illustrated pictorially in Figure 2. We suggest that this pedagogical model even offers insights into the unintended consequences of actions in general life.

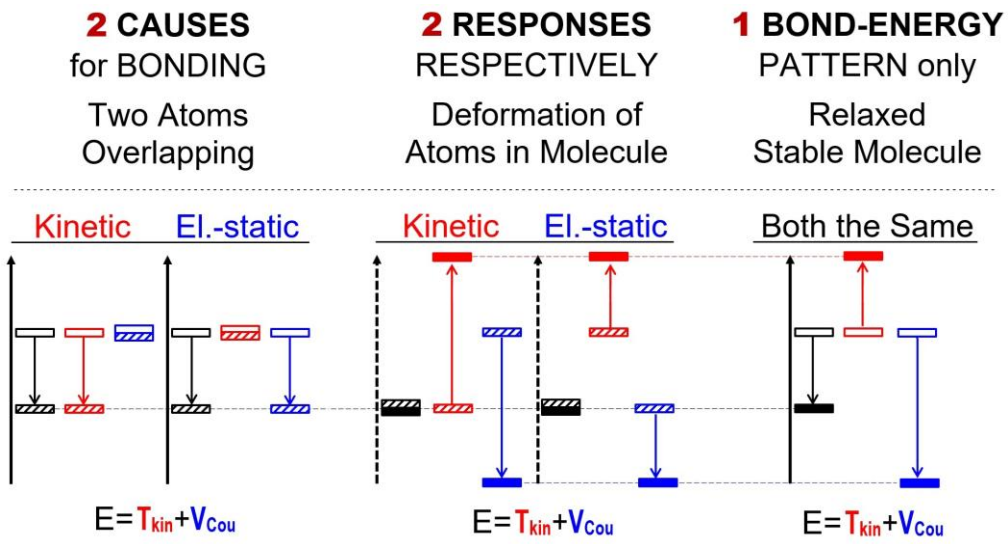


Figure 2. The two different possible causes for chemical bonding. Color code: Red is kinetic electronic energy, Blue is potential energy, Black is total energy. LEFT: Electronic overlap-delocalization reducing the quantum-kinetic energy T_{kin} (less positive), or charge-transfer to the more electronegative atom reducing the electrostatic Coulomb-potential energy V_{Cou} (more negative). MIDDLE: Atoms chemically bonded in the molecule deform according to the laws of physical mechanics, by contracting the wavefunction (quantum-kinetic energy increase) toward regions of low potential (Coulomb-potential lowering), the amounts depending on the original bond-causing perturbation and the sensitivity of the system. RIGHT: The energy pattern in the relaxed bonded molecule is always the same, independent of the cause of bonding, with increased positive kinetic electronic energy, and more negative attractive Coulomb energy.

SUPPORTING INFORMATION

The energy curves for H_2^+ in Figure 1 bear a very close resemblance to the analogous curves published by Nordholm and Bacskay (2020). In Figure 3, our Figure 1 (top) is shown above graphs that reflect the results of Nordholm and Bacskay (2020). The H_2^+ curves have a qualitatively similar appearance to the curves for H_2, also represented in Figure 3 for ease of comparison.

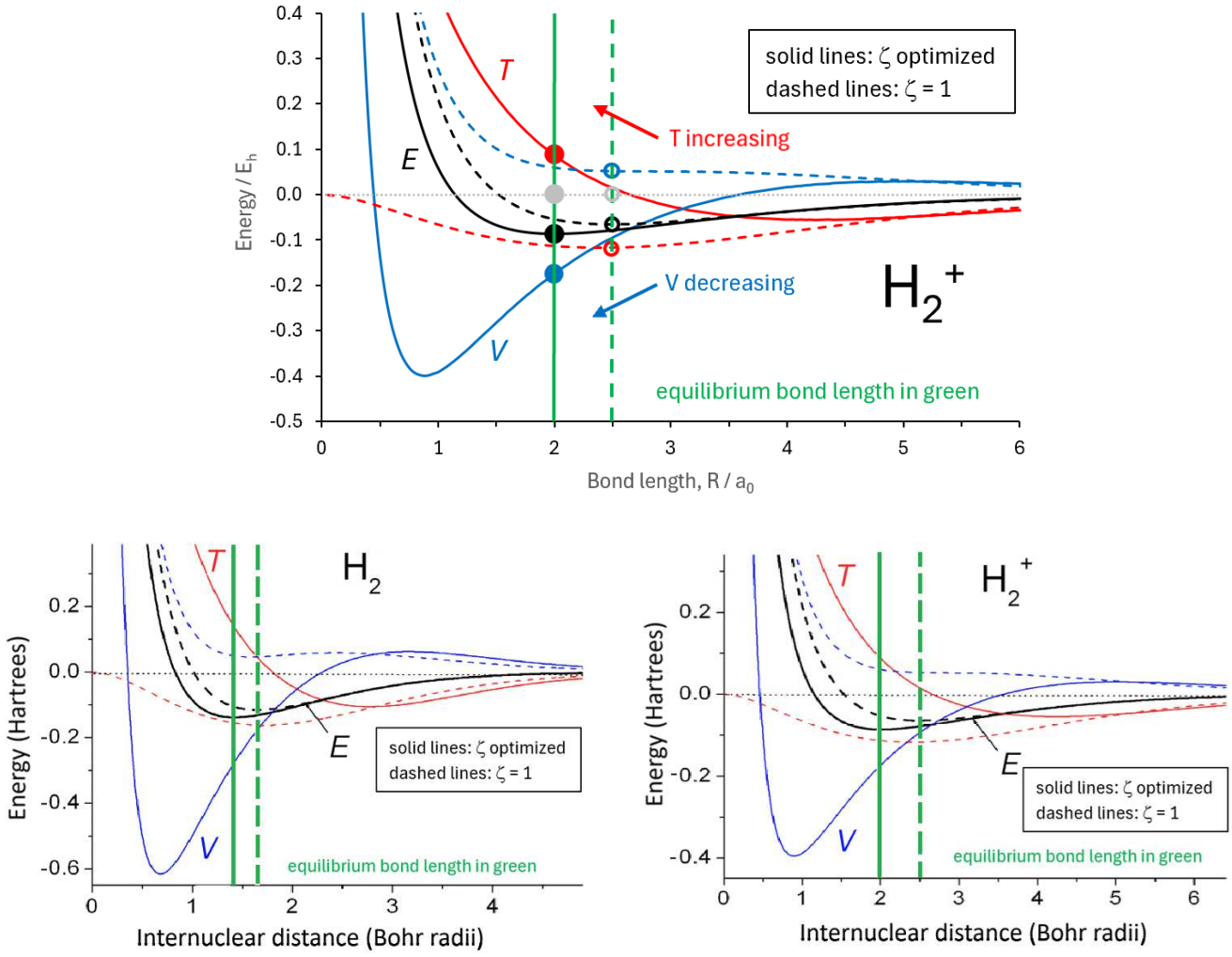


Figure 3. The top graph reproduces the earlier Figure 1. Below, for comparison, are the analogous graphs for H_2 and H_2^+ that reflect the findings of Nordholm and Bacskay (2020).

AUTHOR INFORMATION

Charles S. McCaw
*E-mail: csm@wincoll.ac.uk

ACKNOWLEDGMENTS

CSM wishes to express great thanks to Winchester College for the granting of a sabbatical to pursue this work. WHES gratefully acknowledges support from Siegen (Prof. H. Schönherr) and Tsinghua-Beijing (Prof. Jun Li) universities. Both authors thank Prof. Bacskay for providing further data, and Professors … for illuminating discussions.

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