A dynamical model of the chemical bond: 
kinetic energy resonances between atomic orbitals

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A new approach to chemical bonding is introduced in order to provide an improved understanding of the connection between basic quantum mechanics and the covalent pair bond. Its focus is on the fact that the energy of the bond is largely given by the kinetic energy of the electrons, while the Coulomb forces are only comparable to the kinetic energy terms close to the atomic nuclei, where they define the shape and the size of the atomic orbitals. If atomic orbitals are used as a starting point, the kinetic energy operator is sufficient to determine the energy of the chemical bond. The simple mathematical structure of this operator allows a calculation of bond energy as a function of the distance between the atoms. For Gaussian wavefunctions, it is possible to calculate this bonding potential analytically, determining the bond length, the bond energy and the elasticity of the bond from only a single parameter, the width of the atomic wavefunction. It is shown that the results correspond surprisingly well with experimental values for diatomic molecules.

II. MECHANICAL PROPERTIES OF SINGLE ATOMS: A SIMPLE APPROACH TO UNDERSTANDING COMPRESSIBILITY

Electrons are fermions. They obey the Pauli principle. Therefore, two electrons of the same spin can only occupy the same region of space if they have different momentum. As a result, an increase in electron density requires an increase in kinetic energy and therefore electrons resist compression even if we neglect the Coulomb repulsion. In fact, for high densities, the Pauli principle turns out to be a stronger force of repulsion than the Coulomb forces.

The correct quantitative expression can be derived from the Sommerfeld quantization rule that the density of quantum states in phase space is $\frac{\hbar}{8\pi}$, where $\hbar$ is Planck's constant divided by $2\pi$. The electron spin doubles this density of states, as there are two quantized spin directions for each phase space volume of $\frac{\hbar}{4\pi}$. The minimal energy for a given density of electrons may now be determined by filling the lowest energy regions of phase space and calculating the average kinetic energy $E_{Pauli}$ of each electron as a function of the electron density $\rho$. The result, usually derived as part of the Sommerfeld theory of electrons in metals (for example in chapter 2 of [2]), is:

$$E_{Pauli} = \frac{3\hbar^2}{10m}(3\pi^2 \rho)^{2/3}$$ (1)

where $m$ is the electron mass and $\rho$ is the electron density.

This term, which increases with decreasing distance as $r^{-2}$, prevents the Coulomb attraction, which increases...
The approximation of the Coulomb pressure used is quite complicated. The exact density distributions of the electrons are subject to both quantum mechanical interference effects and complicated screening effects which result from the electron-electron interaction. However, the basic mechanical properties of size and compressibility may be explained without examining these details, just as it is done in macroscopic systems. For this purpose, we need to define a kind of mean field potential for the Coulomb interactions, including electron-electron repulsion.

Effectively, there is one positive charge in the nucleus for each electron. Therefore, we will estimate the Coulomb energy of a given electron density by assuming that the charge of each electron is evenly distributed in a sphere with volume \( V \) around a single positive charge. The Coulomb energy per electron is then given by

\[
E_{\text{Coulomb}} = \frac{3e^2}{8\pi\varepsilon_0} \left( \frac{4\pi}{3} \rho \right)^{1/3}. \tag{2}
\]

Note that by ignoring the electrons which are much closer to the nucleus than most others and therefore see the "naked" charge of the nucleus we have essentially chosen to describe only the valence electrons. In fact, the "nucleus" is effectively an ion with a closed shell. The properties of size and elasticity are not affected by this ion, however, and we can therefore ignore this hidden part of the electronic system in this context. The choice of only a single positive charge for each electron should be best for alkali metals, so quantitative results should be tested by comparison with these elements.

The complete thermodynamic relation for the energy \( E_{\text{el}} \) per electron as a function of the volume \( V_{\text{el}} = \rho^{-1} \) per electron is

\[
E_{\text{el}}(V_{\text{el}}) \approx \frac{3\hbar^2}{10m} \left( \frac{3\pi^2}{V_{\text{el}}} \right)^{2/3} - \frac{3e^2}{8\pi\varepsilon_0} \left( \frac{4\pi}{3V_{\text{el}}} \right)^{1/3}. \tag{3}
\]

The volume occupied by each electron in equilibrium can be determined by finding the minimum of the energy \( E_{\text{el}} \). This minimum is found by setting the derivative \( dE/dV \) to 0. Note, that the volume derivative of the energy is a pressure. Effectively, we determine the point of equilibrium between the Pauli pressure and the Coulomb pressure. In the atom, the electrons are compressed by the Coulomb attraction until the repulsion caused by the Pauli principle compensates this force.

The length scale at which this happens is, of course, the atomic length scale of the Bohr radius \( a_0 \).

\[
a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10} m. \tag{4}
\]

The volume per electron calculated from the relation given above is \( V_{\text{el}} = 2(3\pi^2 a_0^3/5)^{1/3} \approx 4\pi a_0^3 \), roughly equal to the volume of a sphere with radius 1.5\( a_0 \). However, the approximation of the Coulomb pressure used is quite rough, so that only the order of magnitude is meaningful.

To get an idea of the pressures involved, we can now calculate the Pauli pressure and the Coulomb pressure separately to find that for \( V_{\text{el}} \approx 4\pi a_0^3 \), this pressure is around \( 10^{12} Pa \) or 10 million times atmospheric pressure.

To get an idea of how "solid" the atom actually is, we can estimate the compressibility \( K \) of the atom, defined as

\[
K = \left( V \frac{dE}{dV} \right)^{-1}. \tag{5}
\]

Not surprisingly, the result is roughly equal to the inverse Pauli pressure. For \( V_{\text{el}} \approx 4\pi a_0^3 \), we find \( K \approx 5 \times 10^{-12} Pa^{-1} \). This is exactly the order of magnitude found in the compressibilities of the alkali metals. For metals in general, typical values range from caesium at \( 7 \times 10^{-12} Pa^{-1} \) to copper at \( 0.0745 \times 10^{-12} Pa^{-1} \). Note that the compressibility of metals does not depend on the properties of the metallic bond: we are not considering the effects which make atoms stick together yet. To check, whether atoms which form only weak bonds show the same mechanical properties as the atoms of metals, a comparison with the noble gases is useful. The solids formed by condensing the noble gases at very low temperatures have compressibilities from \( 9 \times 10^{-12} Pa^{-1} \) for neon to \( 2.8 \times 10^{-12} Pa^{-1} \) for xenon. This is indeed very close to the alkali metals. Another type of crystal in which the hard sphere model of atoms seems to be appropriate is the ionic crystal. Although the charge distribution in those crystals is very inhomogeneous, their compressibility is only one order of magnitude less than that of the alkali metals and the noble gases, with typical values close to the compressibility of \( 0.42 \times 10^{-12} Pa^{-1} \) for sodium chloride. All values are taken from the corresponding chapters of [2].

The result that the compressibility of single atoms is close to the compressibility of solids is well in tune with the quite intuitive picture of solids consisting of densely packed atoms. As a result of the immense magnitude of the Pauli pressure and the Coulomb pressure, the hard sphere model is quite an adequate picture for the atom despite the misleading notion of emptiness associated with the assumed "sizes" of electrons and nuclei. We can therefore conclude that the source of the low compressibility of solids is indeed the Pauli pressure and that the atomic properties defined by the equilibrium between Coulomb attraction and Pauli pressure are not changed very much when chemical bonds are formed.

However, the Pauli pressure and the Coulomb pressure may be compensated atom by atom, and nothing in this picture makes the separate hard sphere atoms stick together. This is approximately true for the noble gases, but certainly not for most atoms. The periodic table of the elements shows us that the reactivity of the elements depends on the exact number of electrons. Therefore, we need to take a closer look at the particle properties of the electronic system in order to understand the forces that hold atoms together.
III. UNPAIRED ELECTRONS

Since electrons are particles with spin 1/2 and can therefore occupy two spin states for every real space state, the Pauli pressure seems to act separately on two types of electrons. If the electron gas were continuous and did not consist of quantized particles, the spin up density would thus always equal the spin down density, and all matter would be paramagnetic. Indeed, this type of paramagnetism exists in metals and is consequently known as Pauli paramagnetism \[3\].

However, in atoms there are a discrete number of electrons in a discrete number of states. Therefore, it may happen that \(n\) degenerate states are filled with less than \(2n\) electrons. In this case, the Pauli pressure is insensitive to the distribution of the electrons. Indeed, if all unpaired electrons align their spins, the Pauli principle keeps them spatially separate, reducing the electron-electron Coulomb repulsion, while electrons with opposite spins would overlap more strongly, even if in separate real space states. This energy is the spin exchange energy calculated in Hartree-Fock theory. If we have a high degeneracy of states partially filled, we therefore have a ground state with all unpaired spins parallel. This is the reason for both Hund’s first rule and for ferromagnetism.

Energetically, the unpaired electrons are always somewhat unstable, as are all systems with a degenerate ground state, since any small perturbation will remove the degeneracy and break the symmetry of the system by forming new geometric patterns. In surface science, this tendency for forming bonds is often referred to as Jahn-Teller instability \[4\]. Although the change in geometry is not as impressive in the liquid or gas phase, the reactivity of atoms with partially filled shells is a consequence of an instability of the same type.

The effect which causes the perturbation when another similar atom approaches is not, however, the electric field, although van-der-Waals forces will be present. Instead, homopolar bond formation is largely the effect of kinetic energy, as the nearly free electron bands in solid state physics, which are found even in non-metallic systems, suggest. The very small effects of charge density redistribution in a molecule are quite insufficient to explain the energy of chemical bonds, especially since the energetically favorable positions are always the positions close to the atomic nucleus and not the position between the nuclei. In textbooks, this is often explained in a misleading way, because it seems so much harder to visualize the effects of kinetic energy in a picture. If the properties of atoms that the kinetic energy and the potential energy are related by the equilibrium of Pauli pressure and Coulomb pressure are applied to the equations, it is even possible to express the kinetic energy contribution to bonding in terms of the potential energy of the atomic electrons. To avoid this type of confusion, We will therefore neglect van-der-Waals forces and polar contribution altogether and determine the effect of kinetic energy only.

This can also be justified by examining the Hamiltonian of the two atom system:

\[
\hat{H} = \hat{T} + \hat{V}_1 + \hat{V}_2 + \hat{V}_{el-el}
\]

\(\hat{T}\) is the kinetic energy of all the electrons, \(\hat{V}_{1/2}\) is the potential of the respective atomic nucleus, and \(\hat{V}_{el-el}\) is the electron-electron interaction. Considering that due to a negligible overlap of the electron distribution the Coulomb energies, including electron-electron interactions, act almost exclusively on wavefunctions localized at the respective atoms, this Hamiltonian may be separated into atomic Hamiltonians:

\[
\hat{H}_1 = \hat{T} + \hat{V}_1 + \hat{V}_{el-el,1}
\]

\[
\hat{H}_2 = \hat{T} + \hat{V}_2 + \hat{V}_{el-el,2}.
\]

The eigenstates of \(\hat{H}_1\) and \(\hat{H}_2\) are the electronic states of the individual atoms. However, only the potential energy terms are localized at the site of the atom. The kinetic energy term \(\hat{T}\) is the sum of all electronic kinetic energies regardless of the atom at which the electron is located. The total Hamiltonian is therefore given by the sum of the atomic Hamiltonians minus once the kinetic energy term.

\[
\hat{H} = \hat{H}_1 + \hat{H}_2 - \hat{T}
\]

For electronic states located entirely at atom 1, the contributions of \(\hat{H}_2 - \hat{T}\) are negligibly small and so are contributions of \(\hat{H}_1 - \hat{T}\) for states located entirely at atom 2. For delocalized electronic states however, equation \(\hat{H}\) is a useful expression for the evaluation of energy contributions due to the delocalization as we shall see below.

Of course, we have thus neglected the electron-electron interactions between electrons located at different atoms, as well as interactions between an atomic nucleus and electrons located at the other nucleus. For well separated atoms, the net effect of these interactions are the van-der-Waals forces and ionic interactions. We have neglected these effects, because van-der-Waals forces are known to be much weaker than the forces involved in chemical bonding and ionic effects are expected to be weak in the case of symmetric homopolar bonds. To treat the case of polar bonds, the ionic interaction term must be considered in more detail.

Many particle effects within the atoms are still included in the Hamiltonian. However, they do not contribute to the bond energy. The kinetic energy term responsible for the bond formation is generated because the kinetic energy is included in both atomic Hamiltonians, and must therefore be subtracted once from the total. This indicates the fact, that the kinetic energy is not localized at one of the atoms, but causes a delocalization connecting the two atoms.

The kinetic energy is a single particle property. Therefore, we can continue by calculating the energy contributions for each electron separately, adding the energy...
terms of all electrons involved in the bond formation to obtain the total energy. The single particle wavefunctions may be obtained by Hartree-Fock theory, together with the effective single particle Hamiltonian for each atom.

The matrix element connecting two electronic orbitals at different atoms, $|1\rangle$ and $|2\rangle$, is given by

$$
<1|\hat{H}_{eff}|2> = <1|\hat{H}_{1}^{eff}|2> + <1|\hat{H}_{2}^{eff}|2> - <1|\hat{T}|2>,
$$

(10)

where $\hat{H}_{i}^{eff}$ is the effective single electron Hamiltonian of atom $i$. Since $|1\rangle$ and $|2\rangle$ must be eigenstates of the respective atomic Hamiltonians the first two contributions are just the eigenenergies multiplied with the direct overlap $<1|2>$. The latter is a correction for the fact that, since $|1\rangle$ and $|2\rangle$ are not orthogonal, a part of the matrix element represents the expectation value of the Energy of a state localized at one of the two atoms. If the non-orthogonality is removed, this contribution goes to 0, and the remaining matrix element is purely kinetic:

$$
<1|\hat{H}_{eff}|2> = - <1|\hat{T}|2>
$$

(11)

Note, that the sign already suggests a lower energy for the symmetric state!

It is now possible to develop a complete theory of bonding by defining the atomic wavefunctions and their energies and calculating the tight binding matrix elements using only the operator of the kinetic energy.

**IV. BONDING AND ANTI-BONDING STATES**

If we consider only one electronic orbital per atom, the bonding and anti-bonding states of a homopolar bond must be the sum and the difference of the atomic wavefunctions. The energies of the bonding and anti-bonding states can then be determined by calculating the expectation values of the kinetic energy for these two linear combinations. Note, that the sum and the difference of two normalized wavefunctions are automatically orthogonal to each other. If the atomic wavefunctions are given by $\psi_{1/2}(r)$,

$$
\psi_{\pm}(d) = \frac{1}{\sqrt{N_{\pm}}}(\psi_{1}(r + d/2) \pm \psi_{2}(r - d/2))
$$

(12a)

$$
N_{\pm} = 2 \pm \int(\psi_{1}(r + d/2)\psi^{*}_{2}(r - d/2) + \psi^{*}_{1}(r + d/2)\psi_{2}(r - d/2))d^{3}r
$$

(12b)

$$
< E_{kin} >_{\pm}(d) = \frac{1}{N_{\pm}}(< E_{kin} >_{1} + < E_{kin} >_{2} + \frac{\hbar^{2}}{2m} \int(\nabla \psi_{1}(r + d/2))\nabla \psi^{*}_{2}(r - d/2))d^{3}r
$$

(13)

If each atom contributes one unpaired electron, these two electrons can redistribute into the two bonding and two anti-bonding levels as the atoms approach each other. If they pair up in the bonding level, a pair bond is formed. Although these real space integrals already describe the effect of wavefunction overlap on the kinetic energy completely, it is quite revealing to take a look at the same equations in k space by Fourier transforming the whole integral, which represents a convolution of two gradients. In k space, this changes into the integral of the product of the wavefunctions multiplied by $k^{2}$ and a cosine which represents the effect of the real space separation:

$$
\frac{1}{N_{\pm}}(< E_{kin} >_{1} + < E_{kin} >_{2} + \frac{\hbar^{2}}{2m} \int(k^{2}\psi_{1}(k)\psi^{*}_{2}(k)e^{-ikd} + \psi^{*}_{1}(k)\psi_{2}(hkf)e^{+ikfd)})d^{3}k
$$

(14)

If $\psi_{1} = \psi_{2}$, the kinetic energy contributions of the overlapping wavefunctions can be written in an even more compact form:

$$
\frac{1}{N_{\pm}}\frac{\hbar^{2}}{2m} \int(2k^{2}\psi(k)\psi^{*}(k)(1 \pm \cos(kd)))d^{3}k
$$

$$
= \frac{\hbar^{2}}{2m} \int(\psi(k)\psi^{*}(k)(1 \pm \cos(kd)))d^{3}k
$$

(15)

In this case, the kinetic energy distribution is therefore modified by a factor of $1 \pm \cos(kd)$ at each point in k space. If the width of the impulse distribution of the wavefunctions, that is, the width in k space of $\psi^{*}\psi$, is roughly equal to $\pi/d$, the rapid oscillations of the cosine make all overlap contributions cancel (as they should, since the atoms are far apart in real space now). If the k space width is much smaller than $\pi/d$, all parts of the k-space distribution contribute equally and the bonding state is again equivalent to the atomic wavefunction.

The k space distribution of the atomic wavefunction therefore defines a bond length of roughly $\pi$ divided by
its width in k-space, at which the average wavelength of the electron is in resonance with the bond length. Since the k-space width is connected with the real space width by the uncertainty relation, this bond length is roughly equal to the sum of the atomic radii, so the covalent bond is actually strongest when the atoms just about touch each other.

To understand the significance of this result, it should be remembered, that the potential energy effects only enter the picture indirectly, by forming the atomic wavefunctions. The formation of the chemical bond can then be explained entirely by the change of kinetic energy when unpaired electrons begin to tunnel resonantly between the atoms. While the total electron density in real space changes only little, the kinetic energy distribution looses a major part of its high energy contributions.

V. A QUANTITATIVE EXAMPLE: GAUSSIAN WAVEFUNCTIONS

As an analytically solvable example, Gaussian wavefunctions offer a good insight into the formation of bonds by kinetic energy resonance. The most simple bond is a symmetric combination of s-type states:

\[ \psi(r) = e^{-r^2/4\sigma^2} \]  

Since the Fouriertransform of the Gaussian is again a Gaussian, it is easily possible to determine all features of the resulting bond between two unpaired electrons in such atomic states.

\[ \psi(k) = \frac{2\sigma^2}{\pi} e^{-\sigma^2 k^2} \]  

\[ <E_{kin}> = \frac{3\hbar^2}{4m\sigma^2} \]  

Note that the factor of three is a consequence of the three spatial dimensions contributing to the energy. Since we can separate the dimensions for Gaussian wavefunctions, we could as well examine only the one dimensional problem. However, we shall include the constant energy contributions for the sake of completeness.

\[ \psi_+(k) = i\sqrt{\frac{2}{1 - e^{-1/2(d/2\sigma)^2}}} \cos(dk/2)(\frac{2\sigma^2}{\pi})^{3/4} e^{-\sigma^2 k^2} \]  

\[ <E_{kin}> = \frac{\hbar^2}{4m\sigma^2} \left(3 + (d/2\sigma)^2\right) \exp(-1/2(d/2\sigma)^2) \]  

\[ = \frac{3\hbar^2}{4m\sigma^2} - \frac{\hbar^2}{4m\sigma^2} \exp(1/2(d/2\sigma)^2) + 1 \]  

Table 1 lists a few examples of diatomic molecules with their bond length, bonding energy and the elastic constant. Data for the elastic constant was taken from [6] and all other data from [1]. The table also shows the \( \sigma \) values that would correspond to the respective bond properties if the wavefunctions were simple Gaussians. Although there are strong deviations even between different properties of the same molecule, the order of magnitude is reproduced correctly despite the simplicity of the model.

To simulate a directional bond, we can calculate the
bonding potential for two wavefunctions of p-type symmetry:

$$\psi(r) = \frac{x}{\sigma(2\pi \sigma^2)^3/4} e^{-r^2/4\sigma^2}$$  \hspace{1cm} (21a)

$$\psi(k) = 2\sigma k_x (\frac{2\sigma^2}{\pi})^{3/4} e^{-\sigma^2 k^2}$$  \hspace{1cm} (21b)

$$< E_{kin} > = \frac{5\hbar^2}{4m \sigma^2}$$  \hspace{1cm} (21c)

Note, that the separation between the two atoms, d, need not be along the x axis. It is possible to calculate the potential for the additive and the subtractive linear combinations as before. The potential for the bonding state in three dimensions is given by

$$< E_{kin} > = \frac{5\hbar^2}{4m \sigma^2} + \frac{\hbar^2}{4m \sigma^2} \left( \frac{(d_x/2\sigma)^2((d/2\sigma)^2 - 3}{1 - (d/2\sigma)^2) - \exp(+1/2(d/2\sigma)^2) \right. $$

$$+ \left. \frac{(d_y/2\sigma)^2 + (d_z/2\sigma)^2}{\exp(+1/2(d/2\sigma)^2) - 1} \right)$$  \hspace{1cm} (22)

This equation describes a potential with two minima along the x axis, at $d_x = \pm 5.04 \sigma$, as is shown in figure 3. It represents the bonding potential of a $pp\sigma$ bond, since there is rotational symmetry around the x-axis. In the vicinity of these minima, the potential may be approximated by a harmonic potential of

$$< E_{kin} > = \frac{\hbar^2}{4m \sigma^2} \left( 5 - 0.73 + 1.08 (\frac{d_x}{2\sigma} - 2.52)^2 + 0.42 (\frac{d_y}{2\sigma})^2 + (\frac{d_z}{2\sigma})^2 \right).$$  \hspace{1cm} (23)

VI. THE IONIC CONTRIBUTION: EXTENDING THE MODEL TO POLAR BONDS

The kinetic energy only dominates the homopolar bond. In the case of heteropolar bonds, there will be an energy difference between the electronic states at atom A and at atom B, which pulls the electron towards the more electronegative one. In a very simple-minded tight binding approach, this effect may be included as a site dependent energy. With $E_A - E_B = 2D$, the two by two matrix of the polar bond is then given by

$$\begin{pmatrix} T_+ & D \\ D & T_- \end{pmatrix}$$  \hspace{1cm} (24)

$T_\pm$ is the kinetic energy of the bonding and anti-bonding states. For large separations $d$, this is an unrealistic approach, however, since it neglects the energy needed to ionize the atoms and therefore predicts complete ionization as $d$ approaches infinity, not including the Coulomb attraction.

The other extreme is to assume fully polarized atoms. In this case, a term representing the Pauli repulsion is necessary to keep the ions apart. This may be done by adding the bonding and anti-bonding energies for the filled outer shells of the ions.

To combine covalent and ionic effects into a model of the polar bond, it is necessary to consider a total of three possible electronic configurations: state 1, with both electrons at atom A, state 2 with one electron at each atom, and state 3 with both electrons at atom B. Note that this corresponds to a simple extension of Heitler-London theory. The Hamiltonian matrix is

$$\begin{pmatrix} T_+ + T_- + V_A & \sqrt{1/2(T_+ + T_-)} & 0 \\ \sqrt{1/2(T_+ - T_-)} & T_+ + T_- & \sqrt{1/2(T_+ - T_-)} \\ 0 & \sqrt{1/2(T_+ - T_-)} & T_+ + T_- + V_B \end{pmatrix}$$  \hspace{1cm} (25)

For $V_A = +D$ and $V_B = -D$, this is equivalent to the two state model above. However, by including the ionization energy in the $V_{A/B}$, we can now correct the result for large $d$. For very large $d$, $V_{A/B}$ is equal to the total ionization energies $V_{A/B}(\infty)$ required to remove an electron from one atom and add it to the other. $V$ then follows the Coulomb law until the atoms come quite close, when the atomic wavefunctions start to penetrate each other. At very small distances, the difference in energy is given by the energy level difference of the atomic wavefunctions, $D = 1/2(E_A - E_B)$. A transition from the Coulomb regime to the energy level difference regime may be extrapolated using a function of the following form: n

$$V_{A/B}(d) = V_{A/B}(\infty) + \frac{\pm D - V_{A/B}(\infty)}{\sqrt{1 + (d/d_{A/B})^2}}$$  \hspace{1cm} (26a)

$$d_{A/B} = \frac{e^2}{4\pi \epsilon_0 (\pm D - V_{A/B}(\infty))}$$  \hspace{1cm} (26b)

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$$d_{A/B} = \frac{e^2}{4\pi \epsilon_0 (\pm D - V_{A/B}(\infty))}$$  \hspace{1cm} (26b)
The length $d_{A/B}$ defines the length scale at which the transition between covalent and polar bonding occurs. Since this length is largely determined by the atomic size, it is typically close to the bond length. Still, the effect of $V_{A/B}(\infty)$ can often be ignored, since the effects of the energy level difference and the covalent bond combined tend to be stronger at atomic separations equal to the bond length.

VII. CONCLUSIONS

While many textbook explanations of chemical bonds try to visualize the bond only in its spacial distribution, misleadingly suggesting that the source of the bond energy could be the slight increase in electron density between the atoms, the approach presented here clearly identifies the kinetic energy term as the dominant contribution to homopolar bond formation. In the spirit of the tight binding approximation, one can consider the atomic confinement of the electrons as much stronger than the interatomic interactions, and thereby arrive at a bonding potential by simply calculating the expectation values of the kinetic energy for electron pairs evenly distributed between the atoms. This type of bonding potential, which uses only the unchanged atomic wavefunction and the fundamental kinetic energy term of free electrons, not only gives the right order of magnitude for the bond energy, but also reproduces the spatial potential of the bond, with realistic results for bond length and bond elasticity.

Although a quantitatively accurate calculation may only be achieved by including a more detailed description of polar effects than discussed here, it should be pointed out once more, that purely kinetic matrix elements do give highly accurate results in semiconductors and other simple crystals. Furthermore, the free electron behaviour of electrons in metals and the relation between covalent and metallic bonds may be understood better in the light of these considerations. In fact, the major difference between the two type of bonds is not the mechanism of bonding itself, but rather concerns the fact that metallic bonds are not directed as are bonds involving p type wavefunctions. Instead they couple equally well to all neighbours, resulting in the strong delocalization of electrons which makes metals conductors and in their relatively high plasticity compared with the brittle covalent bonds of e.g. semiconductors.

In this manner, it is possible to find numerous connections between the very fundamental laws of quantum physics and the chemical and physical properties of the world surrounding us. Indeed, as technology advances it is important to remember that science not only tells us how to do things, but also why things are as they are, although this often teaches us more about limitations than about possibilities. Even the best artificial materials will not be orders of magnitudes removed from the typical properties dictated by constants such as $\hbar$ and $e$, just as no signal will ever travel faster than the speed of light. However, knowledge of our limitations may often prove more important than know-how, and in this sense, simplified models as the one presented here can prove to be extremely useful.

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[2] Solid State Physics, N.W. Ashcroft and N.D. Mermin, Saunders College Publishing 1976
[3] Froyen and Harrison, PRB 20, 2420 (1979)
[4] see for example Physics of Surfaces, A. Zangwill, Cambridge University Press, page 97, original publication: H.A. Jahn and E. Teller, Proc. Roy. Soc. A161, 220 (1937)
[5] Note, that the anti-bonding state for small $d$ is roughly $k$ times the atomic wavefunction if both atoms are similar. This wavefunction is therefore similar to an excited atomic wavefunction, with the kinetic energy increased accordingly.
[6] Molekülphysik und Quantenchemie, H. Haken and H.C. Wolf, Springer 1992
Table 1 shows the experimentally determined properties of some biatom molecular species, together with the value of the parameter \( \sigma \) which would reproduce this property using Gaussian wavefunctions. Note that despite the simplicity of the model, all values of \( \sigma \) are of the same order of magnitude.

| Molecule | \( Z \) | bond length in \( 10^{-10} \text{m} \) | \( \sigma \) in \( 10^{-10} \text{m} \) | bond energy in kJ/mol | \( \sigma \) in \( 10^{-10} \text{m} \) | bond elasticity in N/m | \( \sigma \) in \( 10^{-10} \text{m} \) |
|----------|-------|-----------------|-----------------|---------------------|-----------------|---------------------|-----------------|
| \( H_2 \) | 2     | 0.74            | 0.23            | 432                 | 0.49            | 520                 | 0.36            |
| \( Li_2 \) | 2     | 2.67            | 0.83            | 110                 | 0.96            | 130                 | 0.50            |
| \( Na_2 \) | 2     | 3.08            | 0.96            | 72                  | 1.19            | 170                 | 0.47            |
| \( N_2 \) | 6     | 1.10            | 0.34            | 843                 | 0.60            | 2260                | 0.32            |
| \( O_2 \) | 4     | 1.20            | 0.38            | 494                 | 0.64            | 1140                | 0.35            |
| \( F_2 \) | 2     | 1.42            | 0.44            | 140                 | 0.85            | 450                 | 0.37            |
| \( Cl_2 \) | 2     | 2.00            | 0.63            | 240                 | 0.65            | 320                 | 0.40            |
| \( Br_2 \) | 2     | 2.28            | 0.71            | 190                 | 0.73            | 240                 | 0.43            |
| \( CO \) | 4     | 1.13            | 0.35            | 1071                | 0.44            | 187                 | 0.55            |
| \( NO \) | 4     | 1.15            | 0.36            | 678                 | 0.55            | 155                 | 0.57            |
| \( HCl \) | 2     | 1.27            | 0.40            | 428                 | 0.49            | 48                  | 0.65            |
Figure 1:
Figure 1a) shows the change in kinetic energy as a function of bond length for the bonding state. The interatomic distance \( d \) is given in units of \( 2\sigma \) and the energy difference from the unbound state is given in units of \( \hbar/4m\sigma^2 \).

Figure 1b) shows the corresponding k-space distributions \( |\psi(k)|^2 \) as a contour plot. The momentum \( \hbar k \) is given in units of \( \hbar/\sigma \).

The minimum in bond energy occurs when the k-space distribution is most narrow, just before the side maxima appear.

Figure 2:
Figure 2a) shows the change in kinetic energy as a function of bond length for the anti-bonding state. All units are as in Figure 1.

For the anti-bonding state, the k-space distribution shows two peaks at small distances \( d \). It is therefore much wider than the bonding state distribution. As \( d \) increases, it narrows, even though side maxima appear.

Figure 3:
Figure 3 shows the bonding potential of the \( pp\sigma \) bond calculated for the p symmetry Gaussian wavefunctions in the xy plane. The unit of length is \( 2\sigma \).
Figure 1:

(a) bonding potential

(b) k-space distribution
Figure 2:

a) anti-bonding potential

b) k-space distribution
Figure 3:

a) contour plot

b) three dimensional representation