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Simple analysis of atomic reactivity: Thomas–Fermi theory with nonergodicity and gradient correction

Received: 8 September 2004 / Accepted: 28 July 2005 / Published online: 15 October 2005
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Abstract Covalent bonding has been found to be related to the relaxation of dynamical constraints on electronic motion in atoms and molecules. The corresponding strain energy in an atom is therefore a measure of its inherent reactivity. Here, such reactivities of the atoms H through Ne are estimated by the use of the Thomas–Fermi density functional theory which can be simply implemented using parametrized exponential electron densities in two different forms—the traditional form assuming complete ergodicity and a modified form which accounts for nonergodicity and therefore strain. The Thomas–Fermi functional is amended by the incorporation of gradient correction of the kinetic energy according to the von Weizsäcker prescription. This correction, implemented within the nonergodic form of the Thomas–Fermi theory, is scaled to yield total atomic energies in agreement with the Hartree–Fock results. The scaling factor shows a variation from around 0.07 for Be to 0.1 for Ne . The reactivity, measured by the stabilization brought by going to the ergodic form of quantization within the Thomas–Fermi theory, is zero for He and Ne and shows a broad peak around oxygen in apparent agreement with chemical intuition. Molecular bonding efficiencies are studied for some small molecules and are found to be relatively large for hydrides and smaller for diatomic molecules such as Be_2 and F_2 .

Keywords Covalent bonding · Atomic reactivity · Ergodicity · Thomas–Fermi theory · Gradient correction

1 Introduction

Atomic reactivity and its expression in the form of molecule formation through chemical bonding is arguably the very heart of chemistry. While ionic bonding is relatively straightforward to explain the more important covalent bonding mechanism is far more subtle. The best simple picture of

covalent bonding is still a matter of debate. Despite the great advances in the computational power of quantum chemistry, it has still not been possible to settle the argument between those favoring kinetic or electrostatic mechanisms as the fundamental causes of covalent bonding. A recent review of the issue and an interesting compromise can be found in the work of Esterhuysen and Frenking [1]. Here, we follow-up an earlier proposal [2, 3] that covalent bonding is best understood as due to a relaxation of dynamical constraints or nonergodicity of the electronic motion by reanalyzing the concept of atomic reactivity. In essence we shall follow the still widely used notion of Lewis [4, 5] that atoms react in order to approach particularly stable inert gas electronic structures more closely. We have found a simple yet plausible way of obtaining atomic energies with or without dynamical constraints, i.e., a way to calculate this Lewis stabilization energy for a simple atom. We thereby identify an inherent reactivity of an atom which, due to the presence of antibonding mechanisms of varying strength, will be partially expressed in a given molecule containing this atom. In this way we hoped to unravel the basic source of covalent bonding from its complex and composite expression in molecular stabilities.

It is now well established that the density functional theories [6–9] which follow the Kohn–Sham [10] approach to the estimation of kinetic energy yield an excellent representation of covalent bonding in molecules. The original density functional theory (DFT) of Thomas [11] and Fermi [12], however, has been shown not to yield any covalent bonding at all [6, 13]. This complete absence of covalent bonding in the Thomas–Fermi (TF) theory of electronic structure is a reliable indication that the mechanism of covalent bonding is contained in the mechanistic complement to the overlap of the Kohn–Sham implementation of the DFT with the TF theory. The essential mechanism introduced by Kohn and Sham in taking over the orbital description of kinetic energy from the Hartree–Fock theory is one-electron dynamics. This account of dynamics is absent in the TF theory which replaces it with a statistically uniform sampling of phase space between bounding energy surfaces determined by the correspondence principle. In doing so the TF theory

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loses all possibility of representing nonergodicity and hindered internal electron dynamics in atoms and molecules. Such dynamical constraints are relaxed upon covalent bond formation by delocalization and facilitation of internal electron dynamics in molecules. Realization of this dynamical origin of covalent bonding goes all the way back to Hellman [14, 15] in the 1930's and Ruedenberg around 1960 [16, 17] who pointed out the fundamental role of valence electron delocalization over covalently bonded atoms. In more recent years the remaining confusion about the role of the virial theorem and the source of the inability of the TF theory to predict covalent bonding has been resolved [2, 3, 18].

The possibility of extending the TF theory to include a quantization based on nonergodic dynamics and a dynamically decomposable phase space has been noted and used to estimate the inherent reactivity of an atom by calculating the stabilization energy associated with the removal of nonergodic constraints on the quantization [2]. The original Thomas–Fermi theory is in this sense unconstrained and ergodic. It effectively treats each atom as if it was of noble gas character, i.e., already reactively relaxed. An examination of the so-defined reactivity of the first ten atoms revealed vanishing reactivity for the inert gas atoms He and Ne, by definition, and a rising reactivity from Li reaching a maximum of 40.8 eV for *O*. The present work is an addendum intended to clarify the previous results and apply the atomic reactivity analysis to the question of bonding efficiencies in some small molecules. One problem of the original analysis is that the Thomas–Fermi theory is quantitatively inaccurate. The reliability of the reactivities that are obtained may therefore be questioned on purely numerical grounds. It is well known that the main flaw of the Thomas–Fermi theory resides in its kinetic energy estimate which only accounts for the orthogonality contribution arising as a consequence of the Pauli principle. The other major source of the kinetic energy of quantum systems is the gradient kinetic energy imposed by boundary conditions on closed systems. The simplest account of such gradient kinetic energy which is the only type present for one-electron ground states is that of von Weizsäcker [19] who noted that it could be estimated directly in terms of squared and integrated electron density. We shall add a von Weizsäcker correction to the functional scaled by a factor λ which will be optimized in a TF calculation incorporating nonergodic spin and angular momentum constraints to yield total atomic energies in agreement with Hartree–Fock calculations. The same functional will then be applied without nonergodic constraints to yield a stabilization that we identify with the atomic reactivity ΔE_{reac} . In this way we shall focus on the two types of kinetic energy broadly termed as orthogonality and gradient kinetic energy which make up the total kinetic energy [19, 20]. The choice of exponential electron densities for each shell with optimized exponents is also related to the type of kinetic energy functional used.

It should be clear that what follows is still mainly a qualitative analysis, but it has been made more quantitative and realistic by attention to the gradient related contribution to the kinetic energy. The concept of atomic reactivity that we use

here is based on the idea that an atom in isolation in its ground state is in an energetically elevated state due to constraints imposed by symmetries and lack of coupling which restrict the electronic motion and thereby cause the Fermi surface, or the chemical potential, to be nonuniform. By our simple comparison of Thomas–Fermi ground state energies with or without such constraints we can estimate the stabilization associated with the removal of these constraints and thereby obtain a measure of the inherent reactivity of the atom. Given such a quantitative measure of atomic reactivity, we then define a concept of bonding efficiency as the fraction of the total atomic reactivity realized as binding energy in a molecule. In an investigation of bonding in small molecules hydrides are found to yield high bonding efficiency while homogeneous diatomic molecules generally yield much lower efficiency.

2 Basic theory

The traditional Thomas–Fermi theory of electronic structure is based on the expression of the energy E as a functional of the electron density ρ -

$$E(\rho) = C \int d\mathbf{r} (\rho(\mathbf{r}))^{5/3} + \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}), \quad (1)$$

where the three terms correspond to, in order, kinetic energy, electron–electron repulsion and electron–external potential energy. In this case the external potential is the Coulomb attraction between the electrons and the nucleus. The constant C is given by -

$$C = \left(\frac{3\hbar^2}{40m} \right) \times \left(\frac{3}{\pi} \right)^{2/3}. \quad (2)$$

If the electron density $\rho(\mathbf{r})$ is optimized fully, the atomic energies will be greatly overestimated due to the lack of gradient correction to the kinetic energy. The kinetic energy represented in the functional above is purely of an orthogonality type, i.e., an estimate in the classical limit of the additional energy required to assign electrons to independent and orthogonal one-electron states. In quantum mechanics another type of kinetic energy is associated with the gradient of the wavefunction as it approaches preset boundary conditions for $r \rightarrow 0$ and $r \rightarrow \infty$. A way to understand this was offered by von Weizsäcker [19] who noted that for a ground state one-electron wavefunction ψ the relation -

$$\psi(\mathbf{r}) = (\rho(\mathbf{r}))^{1/2} \quad (3)$$

can be taken to hold and then the normal quantum mechanical kinetic energy can be rephrased in terms of the electron density as -

$$\begin{aligned}
E_K &= -\frac{\hbar^2}{2m} \int d\mathbf{r} \psi^*(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) \\
&= \frac{\hbar^2}{8m} \int d\mathbf{r} \frac{[\nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r})]}{\rho(\mathbf{r})}.
\end{aligned} \quad (4)$$

If we replace the TF orthogonality kinetic energy functional in Eq. 1 above by this gradient kinetic energy functional, we will get the correct kinetic energy for the hydrogen atom and—apart from the kinetic energy associated with the Coulombic correlation—also the correct kinetic energy for helium. As we go to larger atoms the orthogonality kinetic energy enters and is misrepresented by the gradient functional. Despite its obvious flaws the orthogonality functional is generally used but sometimes with a correction for gradient kinetic energy. It is not a good idea just to add the two functionals, because they substantially overlap and would in a direct sum double count a large part of the kinetic energy. Often the traditional TF functional is corrected for gradient kinetic energy by adding the von Weizsäcker functional scaled down by a factor of 1/9 [6, 21].

Our purpose here is to refine our simple earlier estimate of atomic reactivity by exploiting the simplicity of the von Weizsäcker gradient correction to the kinetic energy. We will add the von Weizsäcker functional multiplied by λ to the traditional TF functional to obtain the new functional -

$$\begin{aligned}
E(\rho; \lambda) &= C \int d\mathbf{r} (\rho(\mathbf{r}))^{5/3} + \lambda \frac{\hbar^2}{8m} \int d\mathbf{r} \frac{[\Delta \rho(\mathbf{r}) \cdot \Delta \rho(\mathbf{r})]}{\rho(\mathbf{r})} \\
&\quad + \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} \\
&\quad + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}),
\end{aligned} \quad (5)$$

which will then be optimized with respect to both ρ and λ , subject to constraints. This simple gradient correction does not account for the kinetic energy accurately in detail, but it provides a major shift to quantitatively reasonable energies sufficient for our present purpose. A similar correction of the Thomas–Fermi kinetic energy was recently used by Parr et al. [21] with good results for inert gas atoms. We shall still take the electron density to be of simple exponential form for each shell [2], i.e.,

$$\rho(r) = \rho_K(r) = Z \frac{\alpha^3}{8\pi} \exp(-\alpha r) \text{ for H and He,} \quad (6)$$

$$\begin{aligned}
\rho(r) = \rho_K(r) + \rho_L(r) &= \frac{\alpha_1^3}{8\pi} \exp(-\alpha_1 r) \\
&\quad + (Z - 2) \frac{\alpha_2^3}{8\pi} \exp(-\alpha_2 r) \text{ for Li to Ne.}
\end{aligned}$$

Here Z is the atomic number. We should note here that the exponential form of electron density would have been exact for hydrogen, if we used the then correct von Weizsäcker kinetic energy as above without any orthogonality kinetic energy. In the presence of such orthogonality kinetic energy and correspondingly reduced gradient kinetic energy obtained by our semiempirical scaling above, the electron density will contract towards the nucleus and a Yukawa form of electron

density -

$$\rho(r) = \frac{C}{r} \exp(-\alpha r) \quad (7)$$

would give a lower energy. We nevertheless stick to the exponential form of electron density specifically to account for the gradient form of kinetic energy which will apply in full both at small r and for large r [20].

As noted in our earlier work [2] the linear electron–nucleus potential energy and the bilinear electron–electron repulsion energy can both be evaluated analytically for exponential electron densities such as we are using. We have -

$$V_{ne} = \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(r) = -\frac{(N_1 \alpha_1 + N_2 \alpha_2)}{2} \quad (8)$$

and

$$\begin{aligned}
V_{ee} &= \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1} \\
&= (N_1 - 1) \widehat{V}_{ee}(\alpha_1, \alpha_1) \\
&\quad + N_1 N_2 \widehat{V}_{ee}(\alpha_1, \alpha_2) + \left[\frac{N_2(N_2 - 1)}{2} \right] \widehat{V}_{ee}(\alpha_2, \alpha_2),
\end{aligned} \quad (9)$$

where N_1 and N_2 are the numbers of electrons in the K and L-shells and -

$$\widehat{V}_{ee}(\alpha_1, \alpha_2) = \frac{1}{2} \frac{(\alpha_1^3 \alpha_2 + 3\alpha_1^2 \alpha_2^2 + \alpha_1 \alpha_2^3)}{(\alpha_1 + \alpha_2)^3}. \quad (10)$$

The kinetic energy terms can likewise be readily calculated analytically for a single exponential form of electron density as for H and He but not for multiple exponential densities as for Li to Ne. Thus, we have employed a simple numerical integration to evaluate the kinetic energies.

3 Thomas–Fermi theory for nonergodic systems

In the discussion above there is no obvious role for electron dynamics. We shall now note that this lack of attention causes a major error that eliminates both atomic reactivity and covalent bonding. Let us first recall the concept of ergodicity by which the nature of classical dynamics can be most fundamentally characterized.

Definition 1 A classical system is ergodic at the energy E if for all trajectories $\Gamma(t; \Gamma_0)$ started on this energy surface at some initial phase space point Γ_0 —except a set of measure zero—the time average of any physical property A in the long time limit reproduces the microcanonical phase space average,

$$\langle A \rangle_{x_E} = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t ds A(\Gamma(t; \Gamma_0)). \quad (11)$$

- This definition implies that ergodic systems show a type of completely coupled statistical dynamics which microcanonically equilibrates the system as time evolves.

The Thomas–Fermi theory is based on the Pauli principle insisting on the grounds of antisymmetry of the total wavefunction that each electron occupy its own unique one-electron state and the correspondence principle stating that a quantum state of a three-dimensional particle motion occupy a phase space volume of h^3 . This correspondence is readily verified for simple systems such as the particle-in-a-box and harmonic oscillator. Thomas and Fermi proposed that -

Proposition 2 *The energy eigenstates of a three-dimensional particle motion can be identified with phase space volumes h^3 occupying classical phase space fully, uniformly and sequentially in the order of increasing energy and the corresponding energy eigenvalues can be obtained as uniform phase space averages of the classical energy in such eigenstate phase space volumes.*

In the normal application of the Thomas–Fermi theory the system has been defined without any consideration of whether it is ergodic or not. The eigenstates implied by the proposition above have therefore been global and delocalized over the entire available classical phase space irrespective of whether the actual dynamics would be correspondingly global and delocalized. There is, however, an inconsistency in this neglect of dynamics which we can understand by considering the case of H_2^+ at very large bondlengths. If the protons are so far apart that the two potential wells presented to the electron are dynamically decoupled, i.e., the electron in its electronic ground state has to be localized in one or the other well, then the ground state energy must clearly be that of a hydrogen atom. Nevertheless, the normal application of the Thomas–Fermi theory would combine the lowest phase space volumes $(1/2)h^3$ on each proton into a lowest quantum state for H_2^+ at long bondlengths. This means that the stabilization associated with covalent bond formation is already fully in place at long distances between the protons and there is no further stabilization to be gained by bringing the protons to short bondlength as in the stable molecule we know from reality. The resolution to this problem lies in the incorporation of dynamical constraints into the Thomas–Fermi theory. We propose to do that by the following addendum to the proposition above.

Proposition 3 Addendum: *For nonergodic systems such that classical phase space is decomposable into dynamically uncoupled subspaces the quantization should proceed separately within each subspace.*

We see now that the extended Thomas–Fermi theory introduced by the addendum above would offer a better description of the unbonded H_2^+ at long bondlengths. There would then be two energy eigenstates of the same energy corresponding to the right or left localized electron in accord with the result of standard quantum mechanics. As the protons are moved closer the dynamical coupling sets in gradually and eventually becomes strong enough for the ergodic version of the Thomas–Fermi quantization procedure to become applicable. In this work we do not offer a description of the gradual onset of bonding which is related to the frequency of

electron transfer between the protons. We can, however, treat the two limiting cases and we shall exploit them to identify the “nonergodic strain energy” which is the ultimate source of atomic reactivity and covalent bonding.

We emphasize now that the reactivity according to our definition is the maximal stabilization associated with the relaxation of nonergodic (or dynamical) constraints on the interatomic electron transfer in a molecule. Since the traditional Thomas–Fermi theory is quantized without any consideration of dynamics it is effectively assuming ergodic and rapid interatomic electron dynamics. By interatomic electron dynamics different spin and angular momentum related subspaces of the bonded atoms are ergodically populated and the energy correspondingly lowered. In order to obtain the reactivity of a single atom, we must therefore modify the Thomas–Fermi theory so as to account for nonergodicity related to spin and angular momentum conservation. We will do this in a simple way by accounting approximately for spin and angular momentum conservation by dividing phase space into l , m_l , m_s -subspaces in which a quantum state occupies a full volume h^3 and not a fraction of h^3 as in the traditional ergodic form of the TF theory. The reactivity can then be obtained as -

$$\Delta E_{\text{reac}} = E_{TF,\text{nonerg}} - E_{TF,\text{erg}}. \quad (12)$$

The new feature here is that the underlying Thomas–Fermi functional that we use will include a von Weizsäcker correction for gradient kinetic energy optimized to yield full atomization energies (in the nonergodic form of the TF theory) in agreement with Hartree–Fock results. In this way we shall obtain more reliable atomic reactivities ΔE_{reac} . We note that the von Weizsäcker correction cannot in detail cure the errors of the Thomas–Fermi functional. Nor is there a well-defined λ -value rigorously founded, but we have obtained a pragmatic solution to the practical problem of large errors in the original Thomas–Fermi theory. One can, of course, further refine the functional to more accurately account for exchange and correlation effects but we shall here focus on the principles and the qualitative content of our results leaving the improvement of accuracy to future refinements [22].

We turn now to the implementation of the nonergodic form of the Thomas–Fermi theory. Let us first consider the case of hydrogen. In the usual ergodic theory half the electron is effectively spin up and the other half is spin down. In the nonergodic theory the whole electron is either spin up or spin down. The kinetic energy can in the latter case be obtained as one-half of the kinetic energy of the helium atom with the same parameter α_1 in the exponent of the electron density function. This procedure captures the fact that the Fermi surface of the spin space containing the electron must be at a level to fit a phase space volume h^3 below it. In the ergodic theory the Fermi surface only fits a phase space volume $h^3/2$ below it in a given spin space. For the atoms Li to Ne we are filling the L-shell and must account for the further subdivision of phase space into parts corresponding to the 2s and the three 2p states. Ignoring the minor 2s to 2p split in energy we treat phase space as subdivided into four equivalent subspaces corresponding to fixed angular momentum.

We begin by evaluating the electronic kinetic energy of He and Ne which will be the same in both forms of the Thomas-Fermi-von Weizsäcker theory. In the traditional ergodic quantization the same functional will, with appropriate choice of atomic number Z , also yield kinetic energies for the other atoms H, Li–F. The interaction potential energies are always evaluated in the same way as described by the functional and analytic integrals above. The kinetic energy of H in the nonergodic quantization is obtained as -

$$KE(H) = \frac{1}{2} KE(He) \quad (13)$$

and that of one of the atoms $Li-F$ as -

$$KE(A(Z)) = \frac{Z-2}{8} (KE(Ne) - KE(He)) + KE(He). \quad (14)$$

In this way the partial occupation of phase space to a higher Fermi surface is accounted for with the result that the kinetic energy is greater than in the case of traditional ergodic quantization.

4 Results

In the case of atoms He and Ne the nonergodic and traditional forms of the Thomas-Fermi theory coincide. We then simply obtain the energy as a function of the exponent α in the electron density of the helium atom by minimizing the energy $E(\alpha, \lambda)$ with respect to α . This yields $\alpha(\lambda)$. We then vary λ so as to find that value which reproduces the Hartree-Fock energy [23] of the helium atom. This is easily done since the energy is a monotone increasing function of λ . In the case of neon we similarly obtain $\alpha_1(\lambda)$ and $\alpha_2(\lambda)$ and then vary λ until the Hartree-Fock energy of Ne is reproduced. The Hartree-Fock energies [23] were calculated using the standard nonrelativistic method and the λ values were optimized to reproduce Hartree-Fock energies to four significant figures. The two-dimensional minimization of energy with respect to $\alpha_1(\lambda)$ and $\alpha_2(\lambda)$ was done by the steepest descent method. In the case of H and the atoms Li to F the same procedure was used except that the kinetic energy was obtained as in Eqs. 13 and 14 above. We thereby obtained atomic energies for H through Ne which by inclusion of both nonergodic quantization and empirical adjustment of the scale factor λ agree with the Hartree-Fock theory. The λ values thus obtained are listed in Table 1 and shown in Fig. 1. We note that for H which in reality has only gradient kinetic energy λ is 0.083. This is a measure of the degree of overlap between the gradient and orthogonality forms of kinetic energy. As we add electrons and charge up the nucleus, the contribution of gradient kinetic energy remains stable with only minor variations. This is in agreement with expectations [21]. Our somewhat low λ values may be partially due to our use of exponential electron densities which are more appropriate for pure Coulomb potentials than for the Yukawa like screened atomic potentials of He through Ne.

Table 1 The optimized scaling factor lambda obtained in the nonergodic quantization for the first ten elements

Atom	λ
H	0.083
He	0.078
Li	0.0757
Be	0.0725
B	0.0755
C	0.0786
N	0.0817
O	0.0882
F	0.09374
Ne	0.0992

Given these λ values we then relax the constraints and quantize the TF theory in the traditional manner corresponding to full ergodicity and rapid electron transfer between spin and angular momentum states. The α values which minimize the energy change slightly and the total energy is lower than in the nonergodic case—except for He and Ne—due mainly to the form of the kinetic energy expression. For each atom we can now obtain a shift in energy downward as listed in Table 2 and shown in Fig. 2. This maximal stabilization energy due to relaxation of constraints is our “atomic reactivity.” We see that it is about 0.3 Hartree for H, zero for He and then rises to a peak of about 1.5 Hartree for oxygen before dropping down to zero again for Ne. The maximum for O reflects that there is both a two-electron hole in the corresponding inert gas structure and a highly charged nucleus. Nitrogen has a three-electron hole but a less highly charged nucleus. It is just slightly less reactive than oxygen. In the case of carbon the charge of the nucleus is too weak and for fluorine there is only a one-electron hole. Thus, the reactivities of these atoms drop down below the level reached by oxygen and nitrogen.

We can now compare the total molecular binding energy [24] with the total reactivity energy. For the molecules BeH_2 and BH_3 the total molecular binding energies were calculated by the program package GAUSSIAN 98 and the G3B3 method was used [25,26]. We define the molecular bonding efficiency as simply the fraction of the theoretically available nonergodic strain energy of the constituent atoms which is obtained as the binding energy of the molecule. Thus, we calculate the ratio of the molecular binding energy and the total nonergodic strain energy obtained by summing strain energies over the atoms of the molecule. The ratios thus obtained will be referred to as the bonding efficiencies and are shown in Fig. 3. We note that the hydrides have higher bonding efficiencies than the homonuclear diatomic molecules which means that the hydrides encounter less antibonding repulsion and more fully relax the dynamical constraints of the separated atoms. We believe one reason for this is that the Pauli repulsion is generally lower for hydrides with few electrons and much higher in homonuclear diatomic molecules and that the molecules B_2 through F_2 have more remaining nonergodicity due to e.g., axial symmetry compared to the corresponding hydrides. If we consider just the hydrides we can see a decrease in bonding efficiency when going from H_2 to

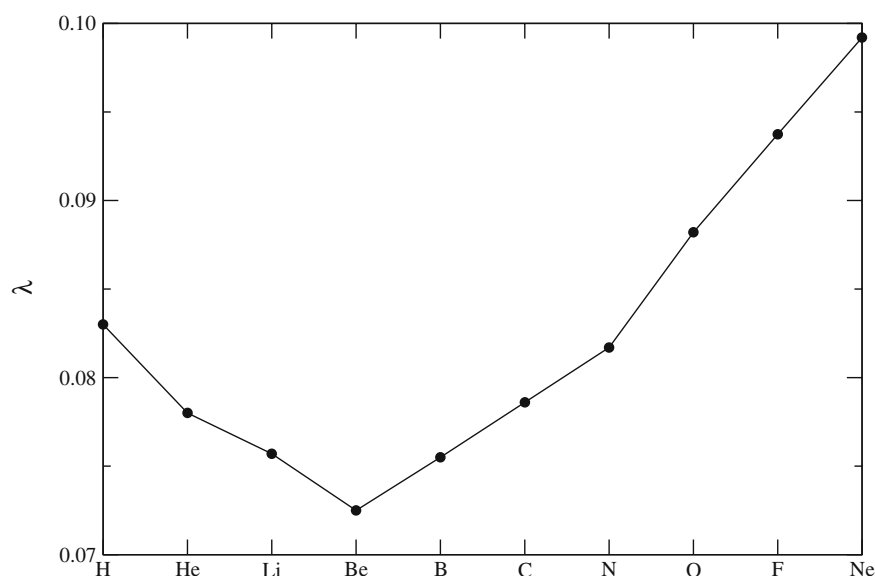


Fig. 1 The optimized scaling factor of the von Weizsäcker correction term to the Thomas–Fermi theory with nonergodic quantization for the first ten elements

Table 2 The atomic reactivity defined as nonergodic strain energy for the first ten elements

Atom	Reactivity (Hartree)
H	0.26
He	0.00
Li	0.10
Be	0.35
B	0.74
C	1.15
N	1.46
O	1.50
F	1.08
Ne	0.00

LiH and from CH₄ to HF which is probably due mainly to rising Pauli repulsion. When going from BeH₂ to CH₄ there is an increase of the bonding efficiency, which may be due to the contraction of the core electron density. If we now, instead, consider the homonuclear diatomic molecules we find a decrease in bonding efficiency when going from H₂ to Li₂ and from N₂ to F₂ which may again be due to Pauli repulsion. When going from Be₂ to N₂ we can see an increase of the bonding efficiency, which may be due to the contraction of the core electron density. In the case of Be₂ the low bonding efficiency could be partially related to a lack of splitting between the 2s and the three 2p states in the TF theory. Clearly the hydrides more fully and uniformly exploit the covalent bonding mechanism which is hindered by strong repulsive forces in the case of Be₂ through F₂.

5 Discussion and conclusion

It is surprising but nevertheless a fact that the successful numerical treatment of covalent bonding by quantum

chemistry has not similarly incontrovertibly resolved the physical nature of the bonding mechanism. Our view that covalent bonding is of quantum mechanical and dynamical origin is but one of several and the issue is clearly not settled [1, 27]. While all views are likely to have some merit the most fundamental ought also to be the most useful. Therefore, we have attempted to draw upon our proposed mechanism to yield a new understanding of atomic reactivity. As is often the case the great flaw of the original and still very relevant Thomas–Fermi theory of electronic structure is very enlightening. In this case the flaw in the theory eliminated the covalent bonding mechanism. By comparison with the Kohn–Sham implementation of the density functional theory, we can then see precisely what it is that must be present in order to account for covalent bonding. The answer is dynamics. We must account for dynamics with its varying degree of constraint. Such constraints impart a reactivity to the atoms and their relaxation is the mechanism of covalent bonding in the deepest sense. This concept of atomic reactivity is precisely that which we allude to when we say that “atoms react in order to more closely approach noble gas structures.” As it turns out the original Thomas–Fermi theory assumes the atoms to be like noble gas interpolations thereby rendering them unreactive. There is, at the moment, no other theory which can produce this type of electronic relaxation energy for the atoms.

In the present work we have refined the estimate of atomic reactivity by adding a von Weizsäcker treatment of gradient kinetic energy adjusted to produce Hartree–Fock atomic energies before the relaxation of constraints. The scaling factor for the von Weizsäcker gradient kinetic energy is close to but slightly smaller than the factor of 1/9 expected by formal gradient expansion. We note that for hydrogen and helium there is really no orthogonality kinetic energy and our results reflect the degree to which the standard Thomas–Fermi

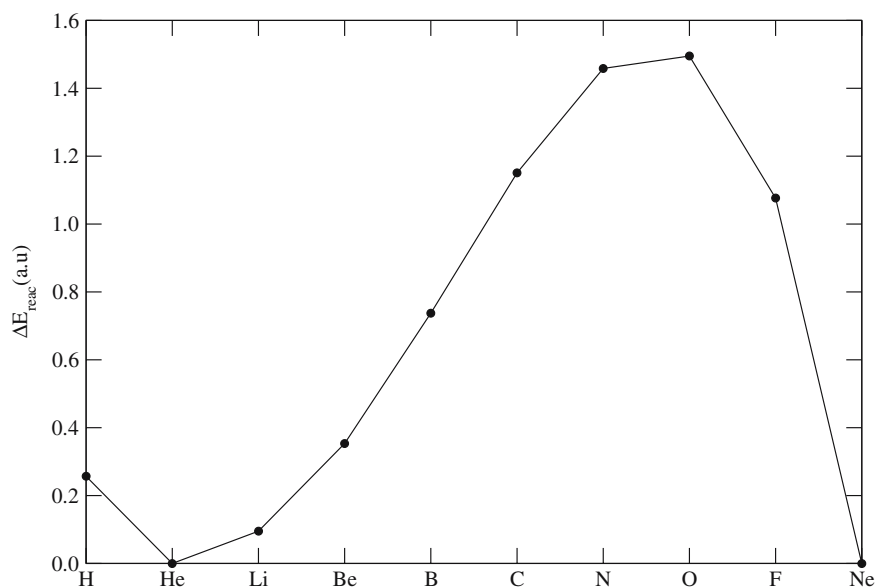


Fig. 2 The atomic reactivity for the first ten elements

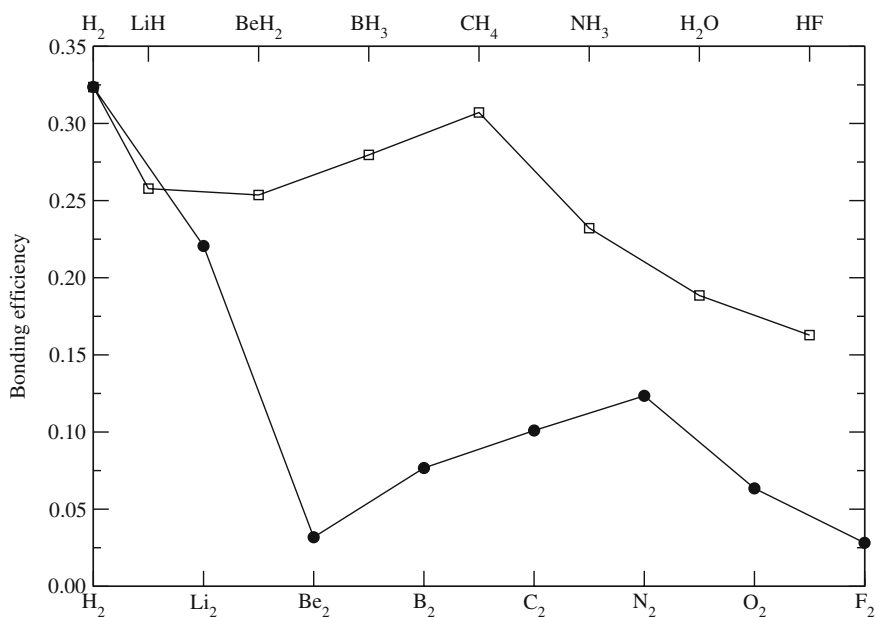


Fig. 3 The bonding efficiency for some homonuclear diatomic molecules and the corresponding hydrides

kinetic energy already captures gradient kinetic energy. For lithium to neon the optimized scale factor remains stable but the orthogonality kinetic energy becomes increasingly dominant. This dominance is most likely to be significantly aided by our choice of simple exponential electron densities for each shell. An unconstrained numerical optimization of the electron density would probably significantly increase λ for the heavier of our ten elements. As it turns out the atomic reactivities that we obtain as a difference of two atomic energies are not very sensitive to the von Weizsäcker correction which is nearly canceled in the subtraction. This is fortunate and supports our use of simple computational methods.

The atomic reactivity obtained behaves in a very intuitive way. It is relatively small for hydrogen, zero for helium and neon. From helium there is a steady rise to the value 1.5 a.u. for oxygen which—quite in agreement with the traditional focus on oxygen and oxidation in chemistry textbooks—is the most reactive atom. Nitrogen is almost as reactive due to its three contributing electrons while fluorine and carbon are noticeably less reactive. The proposed measure of reactivity confirms popular belief and gives it a simple yet deep meaning. It leads to a further concept of bonding efficiency which is the fraction of the reactivity summed up over atoms showing up in the molecule. There are

repulsive mechanisms preventing the full realization of bonding stabilization in molecules. The repulsion between nuclei and between nonbonding electrons are the most obvious. The hydrides are clearly less hampered by such repulsion than our diatomic molecules. Adding hydrogen atoms is clearly the simplest way of bringing a reactive atom toward stable inert gas like electronic structure.

It is noteworthy that our concepts and approach to atomic reactivity relate most directly to the nonpolar covalent bonds rather than the polar covalent bonds which have been the focus of much analysis, e.g., by Sanderson [6,28]. Our work primarily concerns the internal atomic variation in the chemical potential, or Fermi energy, caused by nonergodic or hindered dynamics. There is, of course, also a reactivity related to chemical potentials in separable atoms being different. The chemical potential of an atom A, μ , is essentially equal to the electronegativity of the atom [29] which in turn can be defined by the Mulliken relation -

$$\mu \simeq -E \simeq -\frac{1}{2}(I + E_a), \quad (15)$$

where I is the first ionization energy and E_a is the electron affinity. Given the well-known condition from thermodynamics that the chemical potential of a species at equilibrium shall be the same in all subsystems one is led to the principle of equalization of chemical potential as the fundamental driving force of chemical bonding [6,26]. What we have done here is to take this principle a step further by distinguishing subspaces defined by spin and orbital angular momentum conservation in atoms and noting that covalent bonding is associated with the equalization of chemical potential over such internal atomic subspaces achieved by the dynamical delocalization of valence electrons over two or more atoms. The flexibility of the semiclassical Thomas–Fermi theory has then allowed us to carry out this internal atomic relaxation for an isolated atom as a “virtual relaxation” identifying the final state toward which the dynamical delocalization strives. By this device it has become possible for us to add a numerical estimate of covalent reactivity to the understanding of atoms and chemical bonding. We hope that these concepts and measures might bring the field of chemical bonding theory a step forward by shedding new light on the source of stabilization employed in covalent bonding.

Acknowledgements The authors thank Dr. George Bacskay and Dr. Julia Novakovskaya for useful discussions and the Swedish Science Research Council for support.

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