Atom–Atom Partitioning of Total (Super)Molecular Energy: The Hidden Terms of Classical Force Fields

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Abstract: Classical force fields describe the interaction between atoms that are bonded or nonbonded via simple potential energy expressions. Their parameters are often determined by fitting to ab initio energies and electrostatic potentials. A direct quantum chemical guide to constructing a force field would be the atom–atom partitioning of the energy of molecules and van der Waals complexes relevant to the force field. The authors used the theory of quantum chemical topology to partition the energy of five systems [H₂, CO, H₂O, (H₂O)₂, and (HF)₂] in terms of kinetic, Coulomb, and exchange intra-atomic and interatomic contributions. The authors monitored the variation of these contributions with changing bond length or angle. Current force fields focus only on interatomic interaction energies and assume that these purely potential energy terms are the only ones that govern structure and dynamics in atomistic simulations. Here the authors highlight the importance of self-energy terms (kinetic and intra-atomic Coulomb and exchange).


Key words: quantum chemical topology; atoms in molecules; force field; energy partitioning; coulomb energy; exchange energy; kinetic energy

Introduction

If Moore’s law continues to hold, first-principle simulations of sizeable systems over nanosecond timescales will still not be feasible in the near future. Hence potentials or force fields maintain their role in the prediction of structure and dynamics. Ever since their inception, force fields 1–8 were constructed as a shortcut, that is, a direct relationship between energy and geometry, without strong link to the underlying quantum mechanics. Energy contributions are pragmatically split up in bonded and nonbonded terms, guided by an intuitive blend of intramolecular and intermolecular attributes. In particular, the bonded terms consist of stretch, bend, and torsion contributions and are typically modeled by polynomial expressions. Cross terms are often introduced and Morse-like potentials for substantial bond extensions. On the other hand, the nonbonded terms (1, n interactions where n > 4) are modeled by electrostatic interaction (most often via point charges) and van der Waals type potentials (e.g., Lennard-Jones, Buckingham-Hill). This approach should be contrasted with a generally valid quantum mechanical expression of energy in terms of first and second-order reduced density matrices.9 Here, kinetic energy plays a role, which contrasts with its absence in force fields, or at least, its lack of being explicitly accounted for. Exchange energy does not appear either in classical force fields. When the quantum mechanical energy expression is partitioned into atomic contribution, atomic self-energies arise, which are again hidden in the bonded terms of classical force fields. The central question of this paper is if self-energies can be assumed to be constant, that is, within the framework of quantum chemical topology (QCT).10,11 This theory has been reviewed many times,12–14 which is why we only elucidate salient features in the next section.

In this article we use QCT to partition the energy of five systems [H₂, CO, H₂O, (HF)₂, and (H₂O)₂] into atomic contributions. We distorted these systems from their equilibrium geometry and monitored how the various atomic energy contributions vary upon a change in nuclear coordinates.

To understand better the purpose of this article we spend a few words on outlining its context. The current work is part of a long-term project, which aims at replacing classical point charge force fields. One of the pillars of this (admittedly challenging) project is exhausting the impact of high-rank atomic multipole moments on the quality and reliability of the force field. This is
briefly explained as follows. More modern force fields such as QMFF\textsuperscript{15} use \textit{ab initio} data (energy, forces, and vibrational frequencies) as input for the parameter fitting. Point charges, expressing the electrostatic energy between the atoms of the molecules of the training set, are examples of such parameters. The fitting procedure is an optimization in a typically high-dimensional parameter space leading to many local minima. In principle, this means that one can find more than one value for the point charge associated with a given atom. Although an accurate force field can be obtained for a given molecular training set, it runs the risk of being unsuccessful outside the training set. Reducing the number of fitted parameters would be a good way to tackle this problem. Returning to point charges, one can eliminate them completely from the fitting procedure by replacing them by the (electrostatic) multipole moments of QCT atoms. The burden of achieving a force field that is valid outside the training set then rests on the transferability of the moments. The general philosophy of our force field design is to only fit the energy contributions that cannot be written in terms of QCT. Hence, at the moment, 1,2 interactions (between neighboring covalently bonded atoms) still have to be fitted. However, we recently discovered\textsuperscript{16} the encouraging and perhaps surprising fact that 1,3 and 1,4 Coulomb interactions can be expressed by a converging multipole expansion. This means that the Coulomb interaction between such nearby atoms is treated as a non-bonded interaction rather than as the expected (and traditional) bonded interaction, which is expressed via valence and torsion potentials.

It should be clear that this article straddles force field design on one hand and research on energy partitioning on the other. Both research areas have distinguished histories, with recent examples of the former produced by the Frenking group\textsuperscript{17–20} and the Oviedo group\textsuperscript{21–24} for the latter research area. The design of more accurate force fields also benefits from important developments, for example\textsuperscript{25–30} The current work is not meant to be a comprehensive study in either of these two well-developed areas. Instead, it explores the gap between energy partitioning and the alternatives behind classical force fields. This is why some choices have been made beforehand (e.g., QCT partitioning, level of theory, unrefined integration algorithm) and variations to these decisions are not investigated. However, in spite of this simplicity a clear conclusion emerges.

**Background and Method**

A gradient path is a trajectory of steepest ascent in the electron density $\rho$. Many gradient paths originating at infinity traverse constant-$\rho$ contour surfaces and terminate at a nucleus. Such a bundle of gradient paths carves out a portion of space, which is associated with a topological atom. Details can be found in refs. 10,11. Figure 1 illustrates the four topological atoms appearing in the HF dimer, at three hydrogen bond separations. The hydrogen bonds and the covalent bonds also consist of gradient paths, this time not originating from infinity but from the so-called bond critical points. These are points, where the gradient of $\rho$ vanishes, and where $\rho$ is a minimum along the direction of the atomic interaction line and a maximum perpendicularly to it. Interatomic surfaces mark the atomic boundaries inside the complex and the $\rho = 10^{-3}$ a.u. contour surface the outer boundaries.

The exact total energy of a molecule can be partitioned into one-centre and two-centre atomic components:

$$E_{\text{TOT}} = \sum_A E_{\text{kin}}^A + \sum_{A,B} E_{\text{ee}}^{AB} + \sum_{A,B} E_{\text{ne}}^{AB} + \sum_{A,B} E_{\text{nn}}^{AB}$$  \hspace{1cm} (1)

where A and B run through the atoms of the molecule or van der Waals complex.

Starting with the first group of terms, $E_{\text{kin}}^A$ is the kinetic energy of the electronic distribution of the atomic basin A, defined in eq. (2).

$$E_{\text{kin}}^A = -\frac{1}{2} \int_{\Omega_A} \int_{\Omega_A} \frac{\rho_i(r_1,r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2$$  \hspace{1cm} (2)

where $|r_1 - r_2|$ means that the coordinates are kept separated until the Laplacian has operated on only one coordinate whereupon the coordinates are set equal to each other. This energy is summed over all atoms. Note that this type of term does not involve an explicit interaction between two atoms A and B. The second group of terms, $E_{\text{ee}}^{AB}$, is the total electron–electron interaction energy within a basin (A = B) or between two different basins (A $\neq$ B),

$$E_{\text{ee}}^{AB} = \int_{\Omega_A} \int_{\Omega_B} \frac{\rho_i(r_1,r_2)}{|r_1 - r_2 - r_1 + r_2|} \, dr_1 \, dr_2 \, \rho_j(r_1,r_2)$$  \hspace{1cm} (3)

where $\rho_i(r_1,r_2)$ is the second-order reduced density matrix. The denominator can be identified with the separation between electrons since $r_{12} = |r_1 + r_2 - r_1|$, where $R = R_B - R_A$, and $R_A$ and $R_B$ represent the nuclear coordinates of atoms A and B, respectively. Note that $E_{\text{ee}}^{AB} = E_{\text{ee}}^{BA}$. The third group of terms, $E_{\text{ne}}^{AB}$, is the nucleus–electron interaction energy within a basin (A = B) or between two different basins (A $\neq$ B), as defined in eq. (4)

$$E_{\text{ne}}^{AB} = -\int_{\Omega_A} \left[ \frac{Z_A \rho(r)}{|r - R_A|} \right] \, dr$$  \hspace{1cm} (4)

where $\rho(r)$ is the electronic density at the point $r$ and $Z_A$ is the charge of the nucleus of atom A. Note that $E_{\text{ne}}^{AB}$ and $E_{\text{ne}}^{BA}$ are not equal. Indeed, $E_{\text{ne}}^{AB}$ represents the interaction energy between the nucleus of atom A and the electron distribution of atom B, whereas $E_{\text{ne}}^{BA}$ represents the interaction energy of the nucleus of atom B and the electron distribution of atom A. Finally, the fourth group of terms, $E_{\text{nn}}^{AB}$, is the nucleus–nucleus Coulomb energy.

$$E_{\text{nn}}^{AB} = \frac{Z_A Z_B}{R}$$  \hspace{1cm} (5)

where $R$ is the internuclear distance $R = |R_A - R_B|$. This energy is the same as $E_{\text{nn}}^{BA}$. Note that B cannot be equal to A.
Figure 1. Finite element representation of the topological atoms in the HF dimer, at various F...H separations [(a) 1.5 Å (b) 1.94 Å, (c) 3 Å]. The fluorine nuclei are marked by green spheres, the hydrogen nuclei by white spheres, and the bond critical points by purple spheres. Atomic interaction lines are marked by solid (covalent) or dashed (hydrogen bond) lines. Interatomic surfaces constitute the atomic boundaries inside the complex, while the ρ = 10^{-3} a.u. contour surface denotes the outer boundaries.
This energy includes the electron–electron energy, the nucleus–nucleus energy, and the two electron–nucleus energies \( E_{\text{ne}}^{\text{AB}} \) and \( E_{\text{ne}}^\text{BA} \). To summarize, \( E_{\text{Coul}}^{\text{AB}} \) consists of four terms:

\[
E_{\text{Coul}}^{\text{AB}} = E_{\text{ee}}^{\text{AB}} + E_{\text{ne}}^{\text{AB}} + E_{\text{ne}}^\text{BA} + E_{\text{nn}}^{\text{AB}} .
\]  

(13)

By substituting the first part of eq. (10) into eq. (1) and using eq. (13) the total Hartree–Fock energy can now be expressed as

\[
E_{\text{TOT}} = \sum_A^A E_{\text{kin}}^A + \sum_{A, B} E_{\text{Coul}}^{\text{AB}} + \sum_{A, B} E_{\text{X}}^{\text{AB}} .
\]  

(14)

The basins can coincide (\( A = B \)) and in this case the Coulombic energy between a topological atom and itself, \( E_{\text{Coul}}^{\text{AA}} \), is called the Coulomb self energy. When \( A \) and \( B \) do not coincide \( E_{\text{Coul}}^{\text{AB}} \) is called Coulomb interaction energy. The exchange energy is also decomposed into a self energy \( E_{\text{X}}^{\text{AA}} \) and on interaction energy \( E_{\text{X}}^{\text{AB}} \) with \( A \neq B \). The total self energy, \( E_{\text{self}} \), represents the sum of the intra-atomic energies, as defined in eq. (15)

\[
E_{\text{self}} = \sum_A E_{\text{kin}}^A + \sum_{A, B} E_{\text{Coul}}^{\text{AB}} + \sum_A E_{\text{X}}^{\text{AA}} .
\]  

(15)

The total interaction energy, \( E_{\text{inter}} \), represents the sum of the interatomic energies:

\[
E_{\text{inter}} = \frac{1}{2} \sum_A \sum_{B \neq A} E_{\text{Coul}}^{\text{AB}} + \frac{1}{4} \sum_A \sum_{B \neq A} E_{\text{X}}^{\text{AB}} .
\]  

(16)

Hence, we have that

\[
E_{\text{TOT}} = E_{\text{self}} + E_{\text{inter}} .
\]  

(17)

Finally, from the formulæ above, it is straightforward to show that \( E_{\text{Coul}}^{\text{AB}} = E_{\text{Coul}}^{\text{BA}} \) and \( E_{\text{X}}^{\text{AB}} = E_{\text{X}}^{\text{BA}} \).

The decomposition above has been used before within the QCT framework albeit for different purposes. Mayer and coworkers\(^{1,22} \) used this equation to partition the Hartree–Fock total energy for simple diatomic molecules, applying six-dimensional (6D) integrations for the calculation of the Coulomb and exchange energy within the QCT framework. The Oviedo group applied this approach to several diatomic and triatomic molecules in two recent publications. The first publication\(^{24} \) used the decomposition of the energy to gain insight into the nature of the chemical bond. The group studied the variations of the electronic density in a point \( r \) as

\[
\rho(r) = 2 \sum_i \psi_i(r) \psi_i(r)
\]  

(7)

and the overlap function between two molecular orbitals \( \psi_i \) and \( \psi_j \) as

\[
S_{ij}(r) = 2 \psi_i(r) \psi_j(r).
\]  

(8)

Substituting eqs. (7) and (8) into eq. (6) yields

\[
\rho_2(r_1, r_2) = \frac{1}{2} \rho(r_1) \rho(r_2) - \frac{1}{4} \sum_{ij} S_{ij}(r_1) S_{ij}(r_2)
\]  

(9)

which, when substituted in eq. (3) splits the total electron–electron interaction energy, \( E_{\text{ee}}^{\text{AB}} \), into a Coulomb energy term, \( E_{\text{Coul}}^{\text{AB}} \), and an exchange energy term, \( E_{\text{X}}^{\text{AB}} \).

\[
E_{\text{ee}}^{\text{AB}} = \frac{1}{2} E_{\text{Coul}}^{\text{AB}} + \frac{1}{4} E_{\text{X}}^{\text{AB}} = \frac{1}{2} \int_{\Omega_{\text{A}}} dr_1 \int_{\Omega_{\text{B}}} dr_2 \frac{\rho(r_1) \rho(r_2)}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|} - \frac{1}{4} \int_{\Omega_{\text{A}}} dr_1 \int_{\Omega_{\text{B}}} dr_2 \sum_{ij} \frac{S_{ij}(r_1) S_{ij}(r_2)}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|}.
\]  

(10)

It is convenient to absorb the nucleus–electron interaction, \( E_{\text{ne}}^{\text{AB}} \), and the nucleus–nucleus interaction, \( E_{\text{nn}}^{\text{AB}} \), inside an overall Coulomb term. Doing so, \( E_{\text{Coul}}^{\text{AB}} \) now represents the total Coulomb energy between the charge densities (nuclear and electronic) of two topological basins. We write the total charge density, \( \rho_{\text{tot}}(r) \), as the sum of the nuclear and electronic charge density \( \rho(r) \), correcting for their opposite sign,

\[
\rho_{\text{tot}}(r) = \sum_A Z_A \delta(r - \mathbf{R}_A) - \rho(r)
\]  

(11)

where \( \delta(r) \) is the Dirac function. Hence the total Coulomb energy between two basins A and B is given by

\[
E_{\text{Coul}}^{\text{AB}} = \int_{\Omega_{\text{A}}} dr_1 \int_{\Omega_{\text{B}}} dr_2 \frac{\rho_{\text{tot}}(r_1) \rho_{\text{tot}}(r_2)}{|\mathbf{R} + \mathbf{r}_2 - \mathbf{r}_1|}.
\]  

(12)
advanced post Hartree–Fock wave functions they are in a position to evaluate exchange-correlation energies.

**Computational Details**

To study the effect of bond stretching on the energy components, we used different configurations of CO and H₂. To investigate the effect of angle bending we applied the decomposition scheme to water. We also looked at the variation of the energy components in the HF dimer and the water dimer with respect to the distance between the monomers. The optimum geometries were computed by Gaussian03 at the HF/6-311+G(2d,p) level. The wave functions of the different configurations were determined from single point energy calculations with the same basis set. We modified the program MORPHY98 to compute the self and interaction energies of the Coulomb and exchange contributions via a six-dimensional integration. The Coulomb interaction expressed in eq. (12) is evaluated in practice by computing the electrostatic potential that atom A generates in atom B, which is subsequently multiplied by the charge density of atom B. By swapping atoms A and B in the procedure above one could numerically verify \( E_{\text{Coul}}^{\text{AB}} = E_{\text{Coul}}^{\text{BA}} \). The procedure is the same for the self energy where we equate A to B. One just has to ensure that two quadrature points that are too close do not contribute to the integral, because then \( r_1 - r_1 \rightarrow 0 \) becomes infinite. This situation should also be avoided for the interaction energy, where it can arise between two quadrature points close to the interatomic surface. Finally, all technical comments also apply to the evaluation of the exchange energy with caveat that the "exchange" potential explicitly depends on the molecular orbitals. Because of RAM requirements, the size of the integration grids was limited to about half a million points per basin. Hence, we used the grid \((n_r, n_\varphi, n_\theta) = (90, 40, 60)\) for the \( \beta \) sphere and \((n_r, n_\varphi, n_\theta) = (90, 40, 60)\) for the rest of the basin, where \( n_r \) represents the number of radial quadrature points and \( n_\varphi, n_\theta \) the number of angular quadrature points.

Finally, we clarify the way we report energy contributions in Figures 4, 5, 8, 10, and 12. We subtract the expression of eq. (15) evaluated at one geometry from the one evaluated at another geometry, to give

\[
\Delta E_{\text{self}} = E_{\text{self},2} - E_{\text{self},1} = \sum_A \Delta E_{\text{kin}}^A + \left( \frac{1}{2} \sum_A \Delta E_{\text{Coul}}^{AA} \right) + \left( \frac{1}{4} \sum_A \Delta E_{\text{kin}}^A \right) = \Delta E_{\text{kin}} + \Delta E_{\text{Coul}} + \Delta E_{\text{EXX}} \tag{18}
\]

\[
\Delta E_{\text{inter}} = E_{\text{inter},2} - E_{\text{inter},1} = \left( \frac{1}{2} \sum_A \sum_B \Delta E_{\text{Coul}}^{AB} \right) + \left( \frac{1}{4} \sum_A \sum_B \Delta E_{\text{Coul}}^{AB} \right) = \Delta E_{\text{Coul}} + \Delta E_{\text{EXL}}. \tag{19}
\]

Note that the prefactors \( \frac{1}{2} \) and \( \frac{1}{4} \) for the Coulomb and exchange energies, respectively, have been absorbed in the Δ-

terms on the right hand side of both eqs. (18) and (19). The inclusion of prefactors expresses the weights that the Coulomb and exchange terms have in the total energy difference. Therefore, Figures 4, 5, 8, 10, and 12 faithfully represent the relative importance the various terms have. Second, because of symmetries such as \( E_{\text{Coul}}^{\text{AB}} = E_{\text{Coul}}^{\text{BA}} \), the terms appearing in the double summations of \( \Delta E_{\text{inter}} \) can be regrouped and simplified. For example, in water there are six terms in the double summation, namely, \( \Delta E_{\text{H}1\text{H}2}^{\text{HH}}, \Delta E_{\text{H}1\text{H}2}^{\text{OH}}, \Delta E_{\text{H}1\text{H}2}^{\text{HO}} \), \( \Delta E_{\text{H}1\text{H}2}^{\text{HH}} \), \( \Delta E_{\text{H}1\text{H}2}^{\text{HO}} \), and \( \Delta E_{\text{H}1\text{H}2}^{\text{OH}} \). but \( \frac{1}{2} \sum_A \sum_B \Delta E_{\text{Coul}}^{AB} \) can be compactly written as \( 2 \Delta E_{\text{Coul}}^{\text{HH}} + \Delta E_{\text{H}1\text{H}2}^{\text{HH}} \), where we used the extra symmetry that \( H_1 = H_2 \), since water remains in the \( C_2v \) point group when distorted from equilibrium.

**Results and Discussion**

First we focus on the variation of various energy components with respect to a change in intramolecular coordinates. For that purpose we vary the bond length in CO and H₂ and the bond angle in H₂O. Subsequently, we focus on the same energy components with respect to a change in intermolecular coordinates. The hydrogen bond length will be varied in the water dimer and the HF dimer.

Table 1 presents the complete breakdown of the total energy of CO at equilibrium. The well-documented QCT virial theorem is obeyed with an error of only 0.4 kJ/mol. Correcting the total kinetic energy \( 112.7753 \) au, which is the total energy ("ORIG"). All remaining raw data for CO and the

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The reconstructed total energy ("RECON") is the sum of the self energy ("Total \( E_{\text{self}} \)") and the interaction ("Total \( E_{\text{inter}} \)") energy. "ORIG" is the original Hartree-Fock energy and "error" is the absolute difference between "ORIG" and "RECON" in kJ/mol.
other molecules (Tables S1 to S5) are available as Supplementary Material.

Table 2 shows the exact and reconstructed total energy for CO at different bond lengths. The error changes with the bond length from 8.9 to 13.8 kJ/mol, i.e., a maximum relative difference of 0.040/0.00. The decomposition of H\textsubscript{2} is relatively less accurate (0.23 0/0.00), with an integration error of about 0.7 kJ/mol. The range of this error (4.9 kJ/mol for CO and 0.03 kJ/mol for H\textsubscript{2}) represents a better evaluation of the real error of the decomposition method. Indeed, for our purpose, we are more interested in the variation of the total energy than its actual value.

Turning to individual components, Figures 2 and 3 show how the total energy is partitioned into the self and interaction energy components for CO and H\textsubscript{2}, respectively. Figure 2 clearly demonstrates that the variation of the total energy (\(\Delta E\text{orig}\)) is the outcome of two opposing changes (\(\Delta E\text{self}\) and \(\Delta E\text{inter}\)) for CO configurations very near the equilibrium geometry. The two contributions, \(\Delta E\text{self}\) and \(\Delta E\text{inter}\), are both nearly linear over this narrow range, while their sum, \(\Delta E\text{orig}\), is parabolic, and more than an order of magnitude smaller. As the CO bond is stretched the atoms themselves become more stable but their interaction energy increases (i.e., becomes less stable). The opposite conclusion can be drawn for H\textsubscript{2} (see Fig. 3) provided one inspects a similarly narrow range centered around the equilibrium geometry. Zooming out to a range more than an order of magnitude larger, part of the familiar Morse curve reveals itself. Now all three energy contributions show the same shape, be it shifted. The repulsive wall in the total energy of H\textsubscript{2}, encountered when compressed more than 0.1 Å below its equilibrium bond length, is largely due to the interaction between the hydrogen atoms becoming less favorable (i.e., \(\Delta E\text{inter}\) increases). The main conclusion to be drawn from both Figures is that change in self-energy cannot be ignored. Curiously, most likely all force fields used in atomistic simulations only consist of interaction terms. Hence, the observations made in these two case studies have se-

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rious consequences for the construction of a force field rooted in quantum mechanical energy partitioning.

Figures 4 and 5 illustrate the variations of the kinetic, Coulomb, and exchange components. In both molecules, the kinetic energy behaves similarly: it increases as the bond length decreases, providing the bulk of the repulsion energy. This behavior is repeated for all the systems studied here and can be explained (see Chapter 14 in ref. 35) by means of the Heisenberg uncertainty principle.

Since \( \Delta E_{\text{self}} = \Delta E_{\text{kin}} + \Delta E_{\text{CS}} + \Delta E_{\text{XS}} \) (in the notation of Figs. 4 and 5) the opposite behavior of the self energy in CO versus \( \text{H}_2 \) can be disentangled. In CO, \( \Delta E_{\text{kin}} \) numerically dominates the self energy near the equilibrium, which is only paralleled in \( \text{H}_2 \) for very short bond lengths. The Coulomb interaction is the only component behaving differently between the two molecules. Using \( \Delta E_{\text{inter}} = \Delta E_{\text{CI}} + \Delta E_{\text{XI}} \) one concludes that the exchange interaction is fairly constant in CO and that the total interaction energy is clearly dominated by the Coulomb term. In \( \text{H}_2 \), however, the Coulomb and exchange terms contribute more equally.

As a quick interlude we inspect Figure 6 and Table 3. From the profiles of the exact energy and the reconstructed one we are able to extract the force constant of the bonds by fitting the curve with a second degree polynomial. Figure 6 shows the values of the energy difference and the fitted curve. Ignoring the linear coefficient, we can equate the quadratic coefficient to half the force constant of the bond. From the experimental frequencies of CO and \( \text{H}_2 \), and Hooke’s law, which link these frequencies to the force constants, we are able to compare these values with experiment, as shown in Table 3. There is a close agreement between the force constants obtained from the original and reconstructed energy curves. However, given the limitation of the Hartree–Fock approximation, the experimental force constant for CO deviates by about 20% with the computed values. With \( \text{H}_2 \) there is a closer agreement between the experimental and theoretical force constants.

We now focus on the variation of the different components of the total energy as a function of the bond angle in water. The difference between the original energy and the reconstructed one is constant at 2.2 kJ/mol, with a maximum relative difference of 0.01%/\%0. The total energy is fairly constant with respect to the

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<th>Table 3. Force Constants (kJ mol(^{-1}) (\hat{\text{A}}^{-1})) for CO and (\text{H}_2).</th>
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<td>(v) (cm(^{-1}))</td>
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<td>CO</td>
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\(^a\)From ref. 36.
\(^b\)Derived from fitting the original (unpartitioned) Hartree-Fock energy.
\(^c\)Derived from fitting the reconstructed Hartree-Fock energy.

Figure 5. Variation of the total kinetic energy (\(\Delta E_{\text{KIN}}\)), Coulomb self energy (\(\Delta E_{\text{CS}}\)), Coulomb interaction energy (\(\Delta E_{\text{CI}}\)), exchange self energy (\(\Delta E_{\text{XS}}\)), and exchange interaction energy (\(\Delta E_{\text{XI}}\)) (kJ/mol) of \(\text{H}_2\) with respect to deviation from the equilibrium bond length (\(\hat{\text{A}}\)).

Figure 6. Variation of the total Hartree–Fock energy (kJ/mol) of CO calculated from the reconstructed energy (squares) and from the original energy (circles) with respect to deviation of the equilibrium bond length (\(\hat{\text{A}}\)). The data are fitted with a second degree polynomial. The fitted equations and the correlation coefficients \(R^2\) are displayed in the graph.

Figure 7. Variation of the reconstructed Hartree–Fock energy (\(\Delta E_{\text{RECON}}\)), self energy (\(\Delta E_{\text{SELF}}\)), and interaction (\(\Delta E_{\text{INTER}}\)) energy (kJ/mol) of water with respect to deviation of the equilibrium bond angle (degrees).
bond angle. The variations of its components are plotted in Figure 7 and again in Figure 8 after further breakdown. The analysis of Figures 7 and 8 is analogous to that of Figures 2 and 4 for CO, and Figures 3 and 5 for H₂. Once more, we learn that the self energy plays a crucial role as the HOH angle is varied, since the correct variation of the total energy cannot be recovered from the interaction energy only. From Figure 8, we note that the total kinetic energy behaves again as a repulsion energy, predominately between the hydrogens (see Table S3). However, in this case the Coulomb interaction energy, $\Delta E_{CI} = 2\Delta E_{\text{OH}}^{\text{Coul}} + \Delta E_{\text{HH}}^{\text{Coul}}$, provides an even larger repulsion between all three atoms. The Coulomb energies are the main contributors to the variation of the total self energy and total interaction energy.

Turning to the water dimer, we computed all atomic interactions with the 6D integration, i.e., 6 intra-atomic and 15 interatomic interactions. The absolute error of the reconstructed energy is fairly constant between 23 and 26 kJ/mol. Figure 9 shows the variation of the self energy and the interaction energy. The profiles share a main feature with CO (very near equilibrium). As the hydrogen bond is stretched, the atoms themselves become more stable but their interaction energy increases (i.e., becomes less stable). It is $\Delta E_{\text{inter}}$ that drives the formation of the complex. This finding can be refined by considering Figure 10, which breaks down the energy terms. Clearly, $\Delta E_{CI}$, which is the Coulomb interaction dominates the stabilizing drive toward the water complex. This term is electrostatic in nature and perhaps explains the success of electrostatic models in modeling the hydrogen bond. In the distance range where the hydrogen bond is compressed, Figure 10 shows that the main contributors...
to the change in the total energy are the kinetic energy ($\Delta E_{\text{kin}}$) and the Coulomb interaction energy ($\Delta E_{\text{CI}}$). This inspires us to introduce an extra curve in Figure 9, given by $\Delta E_{\text{RECON}} = \Delta E_{\text{kin}} + \Delta E_{\text{CT}}$. The variation of $\Delta E_{\text{RECON}}$ shows that it is possible to approximately retrieve the minimum energy conformation with only the kinetic and Coulomb interaction energies. However, this graph deviates significantly (by 50 kJ/mol or more), from the exact total energy in the range where the hydrogen bond is elongated, emphasizing the importance of the other energy components such as $\Delta E_{\text{CS}}$. Returning to the surge in kinetic energy upon hydrogen bond compression, we note that this is largely due to the increase in kinetic energies of both oxygens (Table S4).

Finally, we report on the variation of the total energy in the HF dimer. The range of distances is now twice as large as that in the water dimer. The total error ranges from 0.7 to 2.7 kJ/mol, which is much lower than for the water dimer. The energy profiles are plotted in Figures 11 and 12. The variation of the self energy and the interaction energies are the same as those of the water dimer. Again, the variation of the individual components (see Fig. 12) shows that the kinetic energy is by far the most dominant term at short range while all the other terms are attractive. At long range, the Coulomb interaction energy is the larger component. $\Delta E_{\text{RECON}}$ is also able to approximate the variation of the total energy. In this case $\Delta E_{\text{RECON}}$ seriously overestimates the short range energy.

The present work underlines the importance of the self energy for an accurate approximation of the total molecular energy. We are currently working on a calculation method for the intra-atomic energies. This method is based on an inverted one-centre multipole expansion\textsuperscript{37} and if successful would provide a much quicker and more reliable way of computing these energies.

**Conclusion**

We studied the decomposition of the total Hartree–Fock energy into the kinetic, exchange, and Coulomb contributions by means of three-dimensional (one-centre) and six-dimensional (two-centre) integrations over the volumes of topological atoms. The variation of these energies is presented for the bond stretching of CO and H$_2$, the angle bending of water, and the hydrogen bond length variation of the HF and water dimers. The total energy has proven to be the result of an intricate balance between the self energy and the interaction energy. This finding has important consequences for the construction of a parameter-free force field.

The question if self-energies can be assumed to be constant must be answered negatively. This work is a step toward a force field energy function in which the self-energy plays an explicit part.

**References**