# Toward an Experimental Quantum Chemistry: Exploring a New Energy Partitioning

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Ⓢ Supporting Information

ABSTRACT: Following the work of L. C. Allen, this work begins by relating the central chemical concept of electronegativity with the average binding energy of electrons in a system. The average electron binding energy, $\bar{\chi}$, is in principle accessible from experiment, through photoelectron and X-ray spectroscopy. It can also be estimated theoretically. $\bar{\chi}$ has a rigorous and understandable connection to the total energy. That connection defines a new kind of energy decomposition scheme. The changing total energy in a reaction has three primary contributions to it: the average electron binding energy, the nuclear–nuclear repulsion, and multielectron interactions. This partitioning allows one to gain insight into the predominant factors behind a particular energetic preference. We can conclude whether an energy change in a transformation is favored or resisted by collective changes to the binding energy of electrons, the movement of nuclei, or multielectron interactions. For example, in the classical formation of H_2 from atoms, orbital interactions dominate nearly canceling nuclear–nuclear repulsion and two-electron interactions. While in electron attachment to an H atom, the multielectron interactions drive the reaction. Looking at the balance of average electron binding energy, multielectron, and nuclear–nuclear contributions one can judge when more traditional electronegativity arguments can be justifiably invoked in the rationalization of a particular chemical event.
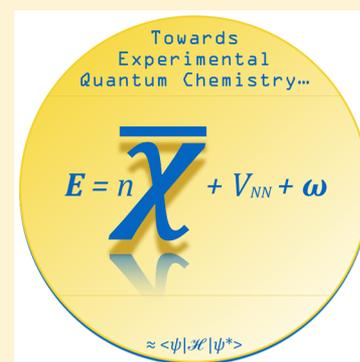
■ INTRODUCTION

Calculating reliably, and understanding, electron–electron interactions has been a continuing challenge for quantum chemistry. In this and subsequent papers we propose a different perspective on this essential component of the energy of a molecule, one offering up the possibility (just that, not certainty) of estimating these from experimental knowledge of spectroscopic data, heats of reaction, and molecular structure. Central to this prospect is a new energy partitioning, with its linchpin being a revived definition of electronegativity as the average electron binding energy.

Electronegativity. Since the dawn of modern chemistry, "electronegativity" has been at its very heart. The story began with Linus Pauling, who defined electronegativity as "The power of an atom to attract electrons to itself" and proceeded to quantify it using bond dissociation energies.[1] The utility of the concept established, this definition was followed by many others,[2–17] maybe most notably that of Mulliken, who defined electronegativity as the average between the ionization potential and the electron affinity,[2] and Parr et al., who introduced a related density functional theory (DFT)-based definition which equates electronegativity with the negative of the chemical potential,[18] in turn approximated by the Mulliken electronegativity.

In this and subsequent papers, we build on the idea of Lee Allen, who defined the concept of electronegativity as the average binding energy of valence electrons in ground-state atoms, which he termed configuration energies (CEs).[10,19–21] The great advantage of Allen's approach is that the CEs are, in

principle, obtainable from experiment, for instance from photoelectron spectroscopy.

Electronegativity has traditionally been attributed to individual atoms and used in understanding the interactions of such atoms.[22] Here the concept is extended, and we will investigate the utility of explicitly considering the average binding energy of all electrons, $\bar{\chi}$, in an atomic, molecular, or extended assembly of atoms. In what follows, ways of attaining this quantity, both in theory and from experiment, will be discussed.

The symbol $\bar{\chi}$ (average electron binding energy) connects to traditional electronegativity, and we will show that $\bar{\chi}$ indeed correlates with traditional atomic electronegativity scales, with certain understandable differences. Electronegativity is in the minds of most chemists inherently related to charge transfer and bond dipoles. Yet, quite often the concept is invoked to rationalize energetic preferences, i.e., observed kinetic or thermodynamic tendencies. One of the objectives of this paper is to show how and when we can know when traditional atomic electronegativity arguments can be justifiably invoked as a rationalization for chemical regularity in energy and when it cannot. The primary utility of the $\bar{\chi}$ definition, as we shall see, is that it allows for the construction of a different energy partitioning and an approach to experimental estimates of electron–electron interactions. We stress that in what follows,

what is most important is the change in $\bar{\chi}$, not its absolute value.

■ DEFINITION OF $\bar{\chi}$

The average binding energy of a collection of electrons ($\bar{\chi}$) is a defined property of any assembly of electrons in atoms molecules, or extended materials:

$$\bar{\chi} = \frac{\sum_i \varepsilon_i}{n} \tag{1a}$$

where ε_i is the energy corresponding to the vertical (Franck–Condon) emission of one electron i into vacuum, with zero kinetic energy, and n is the total number of electrons. For extended structures in one-, two-, or three-dimensions, $\bar{\chi}$ can be obtained from the density of states (DOS) as

$$\bar{\chi} = \frac{\int_{-\infty}^{\varepsilon_f} \varepsilon \times \mathrm{DOS}(\varepsilon)dE}{\int_{-\infty}^{\varepsilon_f} \mathrm{DOS}(\varepsilon)dE} \tag{1b}$$

where ε_f is the Fermi energy. In an insulator, integration to ε_f and to the energy of the highest electronic level will provide identical values of $\bar{\chi}$. This is because there are no levels within the band gap.

Our average binding energy definition for extended structures can be related to the theoretical framework of moments of the electron distribution, so productively used for describing the geometrical factors determining solid-state structure by Pettifor, Burdett, and Lee.[23−26] The average binding energy, $\bar{\chi}$, is the first moment of the energy distribution of a material integrated to the Fermi level.

A related expression for the partial DOS has been found useful for determining the average position of diverse valence states in extended solids and for estimating covalence of chemical bonds.[27,28]

All-Electron vs Valence-Core Partitioning. With our definition (eqs 1a and 1b) in hand we can, if we wish, choose to estimate $\bar{\chi}$ for any subset of electrons, such as "valence-only" (as Allen did).[10] If we do so, however, we invite trouble, for two reasons: (1) the division between "core" and "valence" is not always obvious, especially as one moves down the periodic table, and (2) any such division of core and valence quantities serves to disconnect $\bar{\chi}$ from its rigorous relation to the total energy, as will become clear. Nevertheless, in practical analyses of chemistry, in seeking rationales, it might sometimes prove instructive to focus on a predefined valence set. Computational limitations, such as the utilization of pseudopotentials, or a priori knowledge of poorer descriptions of lower lying levels might also warrant a valence-only approach. A concrete example of how to obtain $\bar{\chi}$ for an atom and a molecule is given in the following section.

■ OBTAINING $\bar{\chi}$

Whereas electrons can be highly correlated in a multiple-electron system and do not always behave as if they were noninteracting, they nonetheless have an average binding energy, which is characteristic of the system. The challenge lies with how to estimate this value as accurately as possible. By definition, the expression of $\bar{\chi}$ only pertains to a "single particle picture" insofar as one can remove single electrons from any system and measure the energy required to do so. In principle, the degree of entanglement (or correlation) of the electrons, which make up the system, does not matter. The definition is

general in the sense that it can be applied to any electronic state (ground or excited). For example, whereas $\bar{\chi}$ for the carbon atom near 0 K may be attributed to the $2p^2$ ($^3P_0$) ground-state configuration, elevated temperatures and the consideration of spin−orbit coupling may merit a weighted $2p^2$ ($^3P/^1D/^1S$) or $2s^1 2p^3$ ($^5S/^3S/^3D/^1D/^3P/^1P$) average instead.

Although both the discrete energy levels of atomic and molecular systems and the effectively continuous densities of states of condensed matter are, in principle, obtainable from experiment, by, for instance, photoelectron (valence) and X-ray (core) spectroscopy, several practical caveats exist.

When estimating $\bar{\chi}$ from a photoelectron spectrum it is necessary either to assume vertical (no nuclear movement) ionization processes, extrapolate these limiting values, or (somehow) obtain a measure of the resulting nuclear relaxation.

In a photoelectron spectrum "shake-up" and "shake-down" satellite bands can arise in cases where ionization occurs from strongly coupled states, typically in the inner-valence or near-core region. Such processes do not show a direct one-to-one correspondence with a molecular orbital (one-particle hole) picture and have been attributed to a "breakdown of the molecular orbital picture".[29−31] In such more complicated ionization processes, one considers the energy difference between an initial state and a superposition of different excited configurations of the resulting cation.

A further complication is that the intensity of different experimental lines may vary with the incident photon (or electron) energy. This effect is diminished for sufficiently high energies; nevertheless accurate interpretation of complex systems may require knowledge of both transition amplitudes and ionization cross sections. In order to assign and interpret more challenging cases it is therefore often necessary to simulate photoelectron spectra using various modern quantum mechanical calculations, each with its own inherent approximations.[32,33]

Fortunately, and as we shall discuss later when addressing the proposed energy decomposition analysis and in subsequent papers, absolute values of $\bar{\chi}$ are not what matters in chemistry. In the analysis of $\Delta\bar{\chi}$ over a reaction many ambiguities relating to the above caveats are expected to diminish due to error cancellation.

There are several technical approaches to estimating $\bar{\chi}$ theoretically. Some of these will be addressed below. The simplest theoretical approximation to $\bar{\chi}$ is arguably the average of the energies of all occupied Hartree−Fock molecular orbitals, which by Koopmans' theorem approximate single electron vertical ionization potentials.[34]

An Example, Methane. If we limit ourselves to the valence electrons, then the value of $\bar{\chi}$ for the ground-state carbon atom calculates (using experimental ionization potentials) as $1/4(2(-18.10) + 2(-11.26)) = -14.7$ eV e^{-1}. If we were to include the 1s core electrons, which are bound by ∼284.6 eV, we end up with the all-electron $\bar{\chi}$ value of -104.7 eV e^{-1}. The value for the hydrogen atom is -13.6 eV e^{-1}.[21]

How do we obtain $\bar{\chi}$ for methane, CH_4? The energy levels of methane have been determined by X-ray photoelectron spectroscopy as -23.1 eV (a_1) and -13.6 eV (t_2).[35] As will be addressed later, similar energies can quickly be obtained computationally using, for instance, long-range corrected density functional theory (LC-DFT), where the orbital energies are calculated as -23.4 and -14.3 eV, respectively. The t_2 levels are triply degenerate. To obtain $\bar{\chi}$ for methane, we simply take the average of these values, $\bar{\chi}_{(CH_4)} = 1/8(2(-23.1) + 6(-13.6))$

$= -16.0$ eV e^{-1}. If we were to include the 1s core electrons of methane, which are bound by $\sim$283.5 eV,[36] we end up with the all-electron $\overline{\chi}$ value of -69.5 eV e^{-1}.

If we consider the formation of CH$_4$ from C and H atoms, i.e., the C + 4H $\rightarrow$ CH$_4$ reaction, we can note that both -16.0 eV e^{-1} (the valence $\overline{\chi}$ value for CH$_4$) and -69.5 eV e^{-1} (the all electron $\overline{\chi}$ value for CH$_4$) are lower than:

$$(4\overline{\chi}_C + 4\overline{\chi}_H)/8 = -14.1 \text{ eV e}^{-1} \text{ (valence only)}$$

and

$$(6\overline{\chi}_C + 4\overline{\chi}_H)/10 = -68.2 \text{ eV e}^{-1} \text{ (all-electron)}$$

The differences in $\overline{\chi}$ over the C + 4H $\rightarrow$ CH$_4$ reaction (i.e., $\Delta\overline{\chi}$) are similar: -1.8 and -1.2 eV e^{-1} for valence-only and all-electron, respectively. This is to illustrate that traditional electronegativity values (such as Allen's) and average all-electron binding energies often provide the same general trends over a reaction and that the inclusion of core electrons does not "marginalize" the importance of valence orbitals in a relative analysis. Instead, the inclusion of lower levels simply offers a more complete description; as we will see, it is needed for the new energy partitioning we introduce. We will return to the relationship between $\overline{\chi}$ of molecules and their constituent atoms; clearly $\Delta\overline{\chi}$ has something to do with the energy change in a reaction.

Comparison with Traditional Electronegativities. Do the average electron binding energies correlate with time-honored measures of electronegativity, for instance Pauling's values? Figure 1 shows the relation for the first four periods. The correlation is clearly there, but with one important difference. By the $\overline{\chi}$ definition, heavier elements will naturally attain larger absolute values of $\overline{\chi}$, simply because the definition includes the cores, i.e., the binding of a larger number of electrons. $\overline{\chi}$ values correlate linearly with normal atomic electronegativity scales (we show a correlation with Pauling χ, but similar ones are obtained with other scales) only along each period, but not down the periodic table. We note that, however, the trend of increasing electronegativity down the periodic table, where each atom of necessity attracts more electrons, is from a certain perspective in accord with Pauling's original definition, as quoted above.

It is $\Delta\overline{\chi}$, i.e., the change in average electron binding energy that is important in this analysis, not absolute values of $\overline{\chi}$. If one wishes to maintain a connection to more traditional electronegativity values, one can estimate $\Delta\overline{\chi}$ using a valence-only approach, i.e., using the Allen scale of electronegativity, which correlates linearly with Pauling's values. As we saw in the CH$_4$ example, such valence-only values of $\Delta\overline{\chi}$ will be similar to $\Delta\overline{\chi}$ estimated with an all-electron approach and, in our experience, lead to the same general conclusions. Because energies of lower levels can, in fact, shift in a reaction, we nevertheless recommend the use of all-electron $\overline{\chi}$ for a more rigorous connection to the total energy.

We understand that the all-electron electronegativities are unfamiliar and seem to run counter to chemistry's fruitful concentration on the valence electrons. We beg the reader's patience; there is a utility to this definition that will reveal itself below.
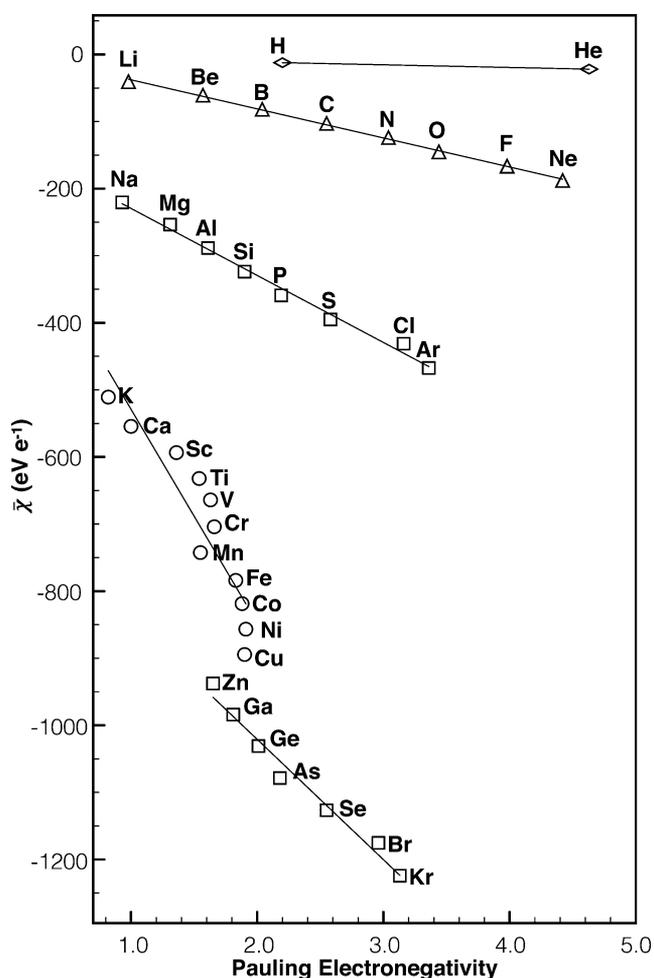

Figure 1. Comparison of $\overline{\chi}$ (from LC-DFT) with Pauling electronegativity for the four first periods.[37] Values for He, Ne, Ar, and Kr are from ref 38. The $\overline{\chi}$ values for H and He are, of course, not zero; they just appear small in value on the $\overline{\chi}$ scale. The lines are linear regression lines for the elements in a period, with a separate line for Zn–Kr.

■ $\overline{\chi}$ IN ATOMS, MOLECULES, AND EXTENDED SYSTEMS

A selection of average electron binding energies is shown in Figure 2, ranging from atoms to molecules and condensed matter. For the atoms, $\overline{\chi}$ increases in absolute magnitude as one moves in a given period to the right in the periodic table. This is a familiar trend that is also seen with any other definition of electronegativity; we noted the correlation with Pauling values above. For molecules, the more electronegative atoms a molecule contains, the lower (larger in magnitude) the $\overline{\chi}$ is. Hexane, C$_6$H$_{14}$, has, for example, a higher value of $\overline{\chi}$ than caproic acid, C$_6$H$_{12}$O$_2$. We include graphene, with its calculated $\overline{\chi}$ of -16.2 eV e^{-1} (valence orbitals only), to illustrate that it can be calculated, just as for a discrete molecule.

After showing examples of how the average electron binding energy may be obtained in a range of cases, we can begin to ask to what degree can changes in $\overline{\chi}$ be related to reactivity, structure, or charge transfer? A careful analysis of the energy change in a chemical transformation is our way into answering this question.
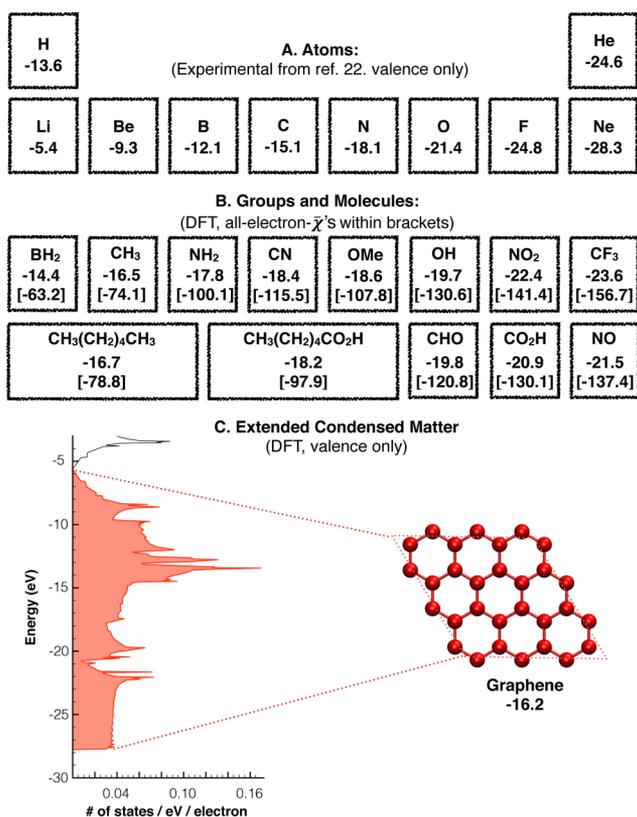
Figure 2. (A) Experimental $\bar{\chi}$ for the valence electrons of first and second period atoms are taken from ref 21. (B) $\bar{\chi}$ calculated for selected molecules. Values where all electrons are considered are given within brackets. (C) $\bar{\chi}$ estimated for the valence bands of graphene.

RELATING $\bar{\chi}$ TO THE TOTAL ENERGY

The idea that orbitals (and their energies) govern chemistry is thoroughly instilled in most chemists today. Important tools, such as Walsh diagrams, and the great success story of frontier molecular orbital theory support an intuitive connection between orbitals and the total energy. Theoreticians have also pointed out several approximate relations of the summed orbital energies with the total energy.[39−41]

In the most general sense, when one ignores rotational, vibrational, and translational contributions, the total energy (E) of any system can be related to $\bar{\chi}$ as follows:

$$E = n\bar{\chi} + V_{NN} + \omega \qquad (2)$$

where $n\bar{\chi}$ is the summed binding energy of all electrons (obtained by some procedure) and V_{NN} is the nuclear−nuclear repulsion energy for a given geometry. The way in which ω represents multielectron interactions will be discussed in detail below. Specific challenges in estimating V_{NN} for an extended system will be addressed in future work. In the remainder of this paper we address only atomic and molecular systems.

In Wave Mechanics. Assuming the Born−Oppenheimer approximation, the Hamiltonian operator for any molecular system can be written as follows:

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{n}\sum_{j>i}^{n}\frac{1}{r_{ij}} + \underbrace{\sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}}}_{V_{NN}} \qquad (3)$$

where n and M are the number of electrons and nuclei, respectively, the first term describes the kinetic energy of

electrons, the second the electron−nuclear attraction, the third the electron−electron repulsion, and the forth the nuclear−nuclear repulsion. Within various independent particle approximations to the solutions of the wave function and energies of this general Hamiltonian, it is possible to identify the terms of eq 2 more specifically. Consider, for instance, the familiar Hartree−Fock energy expression for the total energy:

$$E_{HF} = \sum_{i=1}^{n}\left\langle \phi_i \left| -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} \right| \phi_i \right\rangle + \frac{1}{2}\sum_{ij}(2J_{ij} - K_{ij}) + V_{NN} \qquad (4)$$

where ϕ_i is the spin−orbital of electron i, and J_{ij} and K_{ij} are the matrix elements of the Coulomb and exchange operators, respectively.[34] This expression can be rewritten as

$$E_{HF} = \sum_{i=1}^{n}\varepsilon_i + V_{NN} - \frac{1}{2}\sum_{i<j}(2J_{ij} - K_{ij}) \qquad (5)$$

where ε_i is the eigenvalue of the ith molecular orbital:

$$\varepsilon_i = \left\langle \phi_i \left| -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{Ai}} \right| \phi_i \right\rangle + \sum_{i<j}(2J_{ij} - K_{ij}) \qquad (6)$$

As previously mentioned, one approximation to the average electron binding energy is just the sum of the Hartree−Fock eigenvalues, divided by the number of electrons, n:

$$\bar{\chi}_{HF} = \frac{\sum_i \varepsilon_i}{n} \qquad (7)$$

Note that $\bar{\chi}$ contains electron−nuclear attraction and electron−electron repulsion terms, the latter through the Coulomb and exchange integrals (in HF theory). The total energy E can then be expressed in terms of this average orbital energy, as in eq 8:

$$E_{HF} = n\bar{\chi}_{HF} + V_{NN} \underbrace{-\frac{1}{2}\sum_{i<j}(2J_{ij} - K_{ij})}_{\omega} \qquad (8)$$

where $n\bar{\chi}_{HF}$ is the sum of all one-electron orbital energies. In this framework, ω is an expression of multiple electron interactions, expressed in terms of the same Coulomb and exchange operators that enter $\bar{\chi}_{HF}$. Importantly, ω is negative, a point to which we will return.

The Hartree−Fock definition of $\bar{\chi}$ in eq 7 can be generalized to wave functions that are beyond the mean-field approximation, for instance, that of the complete-active-space self-consistent-field (CASSCF) method. Since occupation numbers in active orbitals in such correlated wave functions are fractional, eq 7 can be generalized as:

$$\bar{\chi}_{MR} = \frac{\sum_i c_i \varepsilon_i}{n \sum_i c_i} \qquad (9)$$

where i now denotes the sum over all optimized orbitals, c_i is the occupation number of each orbital, ε_i is the energy of each orbital, and n is the total number of electrons.

For a discussion on how to extract $\bar{\chi}$ from localized orbitals, and limitations in the process, see the Supporting Information.

In Density Functional Theory. From a practical standpoint is often advisable to forego expensive wave mechanical calculations in favor of DFT. Whereas there is much debate on the meaning of molecular Kohn−Sham (KS) orbitals obtained

with DFT, they nevertheless produce orbital energies and reasonable band structures, which are often in better agreement with experiment than those obtained with Hartree−Fock calculations.[42,43] Reasons for the success of DFT orbital energies have been extensively discussed.[44−50] Within DFT, several technical approaches can be taken to approximate more accurate single electron binding energies. Maybe the most straightforward approach currently is to compute orbital energies using suitable range-separated DFT functionals,[42,51,52] which limit the self-interaction error inherent in DFT by compensating with exact Hartree−Fock exchange at longer distances. First ionization potentials can also be combined with excited-state calculations via TD-DFT to yield good estimates. Statistical averaging of model orbital potentials (SAOP) is another possibility.[45,46]

The interpretation of E is similar in Kohn−Sham density functional theory, where the total energy expression can be written such that,

$$E = n\overline{\chi}_{KS} + V_{NN} \underbrace{- V_{ee}(\rho) + E_{XC}(\rho) - \int \frac{\delta E_{XC}(\rho)}{\delta \rho(r)} \rho(r) dr}_{\omega} \tag{10}$$

where $V_{ee}(\rho)$ is the classical electron−electron Coulomb repulsion energy, E_{XC} is the exchange−correlation energy, $\rho(r)$ is the electron density, and the last term is the exchange−correlation potential.

Note that when the energy is expressed in this manner it becomes possible to decompose ω further, by treating the classical electron−electron Coulomb repulsion $V_{ee}(\rho)$ separately. In fact, experimental determination of the electron density $\rho(r)$, including bonding valence regions, is becoming increasingly realistic with modern synchrotron radiation facilities.[53,54] With the electron density in hand, the classical electron−electron Coulomb repulsion energy, $V_{ee}(\rho)$, can be calculated, given sufficiently accurate data.

Having established the connection between the three key terms $\overline{\chi}$, V_{NN} and ω, in relation to the total energy, we now proceed to discuss how these terms change over the course of a reaction.

■ A NEW ENERGY DECOMPOSITION ANALYSIS

One wants to reason through, in chemistry and in physics, the origins or sources of change in the total energy ΔE. People have used bond energies or Madelung energies coupled with Born−Haber cycles to make sense of ΔE values, productively so. A variety of so-called "energy decomposition analyses", or EDAs, have also been devised. Because of an inherent freedom in how the total energy can be decomposed given an electronic wave function, these are uniquely defined, but are in one way or another, inherently arbitrary in construction. Examples include schemes of Kitaura−Morokuma,[55] Ziegler−Rauk,[56] Mayer,[57] and Frenking and co-workers,[58,59] in addition to a number of others.[60−78]

Our definition of an average binding energy leads us to a different perspective, one that allows for partitioning of changes to the total energy on the basis of experimentally accessible quantities, often without explicit knowledge of the electronic wave function. There is no claim here that our partitioning into $\Delta\overline{\chi}$, ΔV_{NN}, and $\Delta\omega$ is "better"; we will see whether the perspective it provides offers chemical insight.

Understanding ΔE. How can we relate the change in average binding energy of electrons, $\Delta\overline{\chi}$, to ΔE? First, in

approaching ΔE experimentally, one needs to consider the conditions for measurement, which include thermodynamic functions such as the temperature, pressure, and entropy. What ultimately determines the outcome of a chemical event is the Gibbs energy change, ΔG. And it is ΔG (or the Enthalpy, ΔH), which is experimentally measured and compiled in databases, such as the NIST WebBook. Our expression is not for ΔG, but for ΔE. The way ΔE can be estimated from measured changes to ΔG or ΔH is given in the Supporting Information.

Within the Born−Oppenheimer approximation, we can then write the relation:

$$\Delta E = n\overline{\chi} + \Delta V_{NN} + \Delta\omega + \Delta E_{\text{thermal}} \tag{11}$$

Alternatively, the energy change per electron may be written:

$$\frac{\Delta E}{n} = \Delta\overline{\chi} + \frac{\Delta V_{NN}}{n} + \frac{\Delta\omega}{n} + \frac{\Delta E_{\text{thermal}}}{n} \tag{12}$$

where $\Delta E_{\text{thermal}}/n$ sums the changes in rotational, vibrational, and translational contributions to the total energy, over the course of a reaction. These can be accessed from vibrational spectroscopy.

■ FORMING H₂: THE SIMPLEST REACTION

The chemical bond is central to understanding chemistry, and we turn first to the analysis of a familiar example. The formation of H_2 from atomic hydrogen is commonly described simply either by a Heitler−London (VB) coupling of two H atoms, or, in molecular orbital terms, by the constructive interference of two hydrogen 1s states, producing a bonding σ-state (Figure 3). Of course, one moves beyond these simplistic
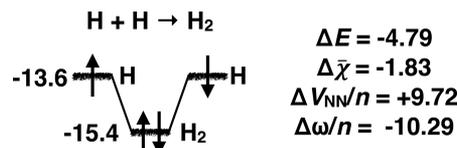
Figure 3. Lowering of electron binding energies, or the stabilization of orbitals, dominates the formation of H_2 from atomic hydrogen. All energies are calculated from experimental values provided by the NIST Chemistry WebBook and are given in electronvolt per electron (eV e^{-1}), except for ΔE, which is given in electronvolt (eV).

starting points in ways familiar to the community, to obtain good wave functions describing observable properties of the molecule or ion. In all of the following examples we will sidestep the complexities of quantum mechanical calculations and proceed solely using accurate experimental data.

With knowledge of the experimental heat of formation (+2.259 eV) and ionization potential (−13.598 eV) of the hydrogen atom and the ionization potential (−15.426 eV), bond distance (0.7414 Å) and the fundamental stretching frequency of molecular hydrogen (4401.2 cm^{-1}), we can describe the elementary reaction of H_2 formation from two hydrogen atoms (Figure 3). In order to allow for meaningful comparison between systems of different size, in the examples that follow, it becomes useful to discuss energies with the aid of eq 12, i.e., energy per electron. As such $\Delta\omega/n$ and $\Delta V_{NN}/n$ express energy change over a reaction in the same units as $\Delta\overline{\chi}$, namely in eV e^{-1}.

Because the bound state of H_2 lies lower in energy than the atomic state, $\Delta\overline{\chi}$ for this reaction is $-15.426 - (-13.598) = -1.83$ eV e^{-1}. If this average value is multiplied by the total

number of electrons, $n\Delta\bar{\chi} = 2(-1.83) = -3.66$ eV, we get a value reasonably close to the enthalpy change of the reaction, -4.52 eV.

What about the other terms, $\Delta V_{NN}/n$, $\Delta\omega/n$, and $\Delta E_{thermal}$ in this reaction? A large and positive value of $\Delta V_{NN}/n = +9.71$ eV e^{-1} arises, due to the increased nuclear−nuclear repulsion associated with bond formation. $\Delta E_{thermal}$ is small, and we can quickly approximate it from the harmonic vibrational energy at 0 K, $\Delta E_{ZPE} = +0.27$ eV. Assuming knowledge of all other terms (ΔE, $\Delta\chi$, ΔV_{NN}, and $\Delta E_{thermal}$), $\Delta\omega/n$ is straightforwardly obtained from eq 12. Note that this estimate of an electron−electron interaction is based entirely on experimental observables. For the 2H → H_2 reaction $\Delta\omega/n$ equals -10.29 eV e^{-1}, which largely compensates the repulsive $\Delta V_{NN}/n$ energy. As will be seen in general when $\Delta\omega/n$ and $\Delta V_{NN}/n$ terms are both large compared to $\Delta\bar{\chi}$, the two will largely cancel each other. How can they cancel when in both of them there is repulsion (electron−electron and nuclear−nuclear, respectively)?

■ INTERPRETATION AND USE OF ΔV_{NN} AND $\Delta\omega$

The ω is so important in some reactions, and its definition in our work is an unfamiliar one. So it is worthwhile to find still other words to express the way this multielectron interaction term behaves. It is crucial to realize that ω, as defined in eqs 8 and 10, contains the negative of the electron−electron repulsion and the positive exchange and correlation energy. This "reversal" of sign of the electron−electron repulsion when it enters ω is a consequence of expressing the total energy as a function of $\bar{\chi}$ in eq 2 and is necessary to avoid "double counting" the electron−electron interactions. Thus, when $\Delta\omega/n$ is more negative, electron−electron repulsion is increased, and vice versa. In other words, when the $\Delta\omega/n$ term is large and negative, the electron−electron repulsions are more positive (greater) in the molecule, but $\Delta\omega$ contains the negative of these repulsions. The hydrogen formation discussed above is only one pertinent example of this.

In general, we can consider the process of any two atoms being brought closer together. As a consequence of increased nuclear−nuclear repulsion, $\Delta V_{NN}/n$, electrons rearrange to shield the repulsion of the two approaching nuclei. This rearrangement on average forces the electrons closer in-between the nuclei, where they experience a stronger electron−nuclear attraction, which is stabilizing and internalized in $\Delta\bar{\chi}$. The necessary rearrangement of electrons simultaneously increases electron−electron interactions, which are destabilizing overall. In $\Delta\omega/n$ however, this quantity appears with the reversed sign. As such, $\Delta\omega/n$ is a quantification of changing electron−electron interactions. These include the classical electron−electron repulsion, exchange interactions (which equal zero in the case of H_2, as its two electrons are of opposite spin), and correlation effects. The above arguments are couched in terms of potentials; of course the virial theorem allows a parallel analysis in terms of kinetic energies.

The nuclear repulsion energy, V_{NN}/n, is a direct consequence of molecular structure. In the course of a reaction or physical transformation $\Delta V_{NN}/n$ can be large, compared to changes in $\Delta\bar{\chi}$. The magnitude of $\Delta V_{NN}/n$ is especially sizable in the formation of chemical bonds, and multiple examples of this will be given in the second paper of this series. By itself $\Delta V_{NN}/n$ offers one way of quantifying geometric change. For instance, if one considers two geometric conformers, $\Delta V_{NN}/n$ calculated

between them becomes one nonelectronic expression of their relative compactness. For transition states it is commonplace to classify competing geometries as either "loose" or "tight", depending upon arbitrary bond lengths and angles. $\Delta V_{NN}/n$ offers a straightforward relative quantification of how "loose" or "tight" each conformation is.

An alternative to $\Delta V_{NN}/n$ and $\Delta\omega/n$ might be their sum, $\Delta(V_{NN} + \omega)/n$, which describes how well changing nuclear−nuclear repulsions are screened by changing multielectron interactions. $\Delta(V_{NN} + \omega)/n$ is that part of ΔE that is not $\Delta\bar{\chi}$ controlled. Such a simpler compact presentation might be advantageous if the sole focus of an energy analysis were $\Delta\bar{\chi}$ (or orbitals). One other instructive quantity is the ratio of $\Delta\bar{\chi}$ contributions to the sum of the absolute values of $\Delta\bar{\chi}$ and $\Delta(V_{NN} + \omega)/n$ contributions, i.e., the definition of eq 13. The latter provides a straightforward measure of what percentage of the total energy change is controlled by orbitals $\Delta\bar{\chi}$, and how much is controlled by $\Delta(V_{NN} + \omega)/n$.

$$\Delta\bar{\chi} \text{ "contribution"}(\%) = \frac{100 \times |\Delta\bar{\chi}|}{|\Delta\bar{\chi}| + |(\Delta V_{NN} + \Delta\omega)/n|}$$

(13)

Looking again at the example of hydrogen formation (Figure 3), the combined term $\Delta(V_{NN} + \omega)/n = -0.57$ eV e^{-1}. If we at the same time consider that $\Delta\bar{\chi} = -1.83$ eV e^{-1}, this example of "covalent"-bond formation appears in tune with the expectations of most chemists, that orbitals govern reaction outcomes. By eq 13, 76% of the interaction energy is due to the stabilization of orbitals (an increased electron binding energy). Below we will give examples where this almost intuitive impression of orbital interactions can be misleading and where changes in the average binding energy of electrons, $\Delta\bar{\chi}$, and the total energy change can take on opposite signs.

■ WHERE ORBITALS DO NOT GOVERN

Electron Attachment. One simple example of a very different makeup of stabilization may be found in the reaction of a hydrogen atom with an unbound electron to form the hydride anion, H^- (Figure 4). With knowledge of the experimental electron affinity (+0.754 eV)[79] of the hydrogen atom, we can compare this process to the H_2 formation addressed earlier.

H + e^- → H^-

0.0 ⋯ e^-

-0.8 H^-

-13.6 H

$\Delta E = -0.75$
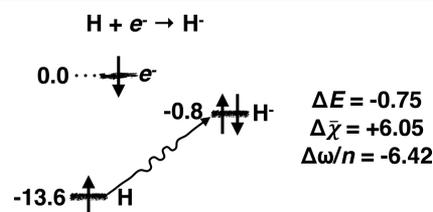$\Delta\bar{\chi} = +6.05$
$\Delta\omega/n = -6.42$

Figure 4. Hydrogen's favorable electron attachment is not orbital controlled, but is enabled by multielectron interactions.

Here $\Delta\bar{\chi}$ is large and positive, + 6.0 eV e^{-1}. The 1s orbital energy of H goes up substantially on binding an electron. At the same time the reaction is exothermic by −0.75 eV. From eq 11 we see that if $\Delta E < 0$ while $\Delta\bar{\chi} > 0$ and $\Delta V_{NN} = 0$, then $\Delta\omega$ is what determines the reaction outcome. The $\Delta\bar{\chi}$ contribution is negative relative to the overall total energy change, amounting (by eq 13) to 48%. Consequently, it is the introduction of multielectron interactions that enables this reaction.

Ionization of H₂. Let us consider another simple ionization. Due to a complete absence of multielectron interactions, we can calculate $\bar{\chi}$ for H_2^+ in the following manner: First, the experimental bond length (1.052 Å) enables calculation of the nuclear−nuclear repulsion energy to 13.688 eV. By combing the known bond energy of H_2^+ (2.651 eV) with the nuclear−nuclear repulsion energy and the ionization energy of the hydrogen atom (13.598 eV), $\bar{\chi}$ calculates as $-13.688 + -2.651 + -13.598 = -29.937$ eV. Using this value we can proceed to investigate the $H_2 \rightarrow H_2^+ + e^-$ reaction. The $\bar{\chi}$ value for an unbound electron is zero. The unfavorable change in average binding energy ($\Delta\bar{\chi} = 0.46$ eV e^{-1}) is small compared to the favorable change in $\Delta V_{NN}/n$, of -2.87 eV e^{-1}. Note that here the $\Delta\bar{\chi}$ contribution to the total energy change is only 6% (by eq 13) and that the majority of the energy change is due to the removal of multielectron interactions, which amount to 10.285 eV e^{-1}. Notice that $\Delta\omega/n$ is positive, whereas earlier $\Delta\omega/n$ was negative. In this ionization, there is no electron−electron interaction in the product cation. The neutral molecule, which, of course, has significant electron−electron repulsion (negative ω) is on the left side of the chemical equation.

Helium! Helium is analogous to H^- in that the number of electrons is the same (two), the nuclear−nuclear repulsion is nonexistent and electron−electron interactions are present (Figure 5). Again, we can rely on accurate experimental data.
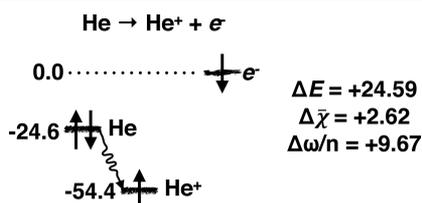

Figure 5. Ionization of helium is disfavored by all terms in the energy expression.

The first and second ionization potentials of helium, 24.587 and 54.418 eV, are good approximations to $\bar{\chi}$ for He and He$^+$, respectively. The first ionization potential also equals ΔE for the ionization process $He \rightarrow He^+ + e^-$. This allows calculation of $\Delta\bar{\chi}$ as $+2.62$ eV e^{-1} and of $\Delta\omega/n$ as $+9.67$ eV e^{-1} for the ionization process.

■ CLASSIFYING REACTIONS

By eq 11 and 12, there are eight possible combinations of $\Delta\bar{\chi}$, ΔV_{NN}, and $\Delta\omega$ that can describe any exoergic or endoergic transformation. These reduce to three main classifications, to which the labels binding, nuclear and multielectron, each are assigned with the suffix favored or resisted (Table 2). Favored and resisted implies that the preceding term is the only one out of the three ($\Delta\bar{\chi}$, ΔV_{NN}, and $\Delta\omega$) that favors, or resists, a given transformation. That covers six of eight possibilities; if all terms

contribute with the same sign, we term the reaction as either a relaxation or deformation.

In addition to these four cases, a transformation can be simultaneously favored or resisted by changes to the vibrational, rotational, and translational energy contributions to the total energy change, $\Delta E_{thermal}$ (eqs 11 and 12). Quite aside from ΔE, any transformation can, of course, also be governed by changes in the external pressure, via a pV term, or by the changes in entropy, through a TS term. We would refer to such situations as being "induced by pressure" or "entropy driven", respectively.

By the classification scheme outlined in Table 2, our first example of dihydrogen formation is exoergic and nuclear-resisted, whereas hydride formation is exoergic and multi-electron-favored. As we will see in a more inclusive study of chemical bonding in a subsequent paper, the latter classification will surface again, when describing polarized (ionic) diatomic bonds. Contrary to ionization of the hydride anion, $H^- \rightarrow H + e^-$, which classifies as multielectron-resisted (the reverse of entry 2 in Table 1), the nuclear movement in the $H_2 \rightarrow H_2^+ + e^-$ reaction, instead leads to its classification as nuclear-favored. In our last example, that of helium ionization, the ΔV_{NN} term is absent, and all contributions to the total energy change are positive. That reaction is therefore classified as a deformation. The reverse process can be considered a relaxation.

In practice, the eight main typologies for decomposing ΔE, shown in Table 2, are not likely to be found in equal measure.

Table 2. A Classification of Chemical and Physical Transformations[a]

$\Delta\bar{\chi}$	ΔV_{NN}	$\Delta\omega$	classification
−/+	−/+	−/+	relaxation/deformation
−/+	+/−	+/−	binding-favored/resisted
+/−	−/+	+/−	nuclear-favored/resisted
+/−	+/−	−/+	multielectron-favored/resisted

[a]Three terms influence the change in energy, ΔE; "+" and "−"denotes positive and negative energy contributions, respectively.

Subsequent papers will demonstrate that the two nuclear and two multielectron classes are common examples in chemistry. The binding classification requires ΔV_{NN} and $\Delta\omega$ terms of equal sign, which is more rare. This may occur if net movements of nuclei are small, which allows for changes to exchange and correlation energies to dominate over coulomb repulsion in, for instance, near vertical photoexcitations. Except for frozen geometries, we have not yet conceived of a situation where the relaxation/deformation classification applies. It might be that this convergence can occur in special cases, for instance when a small rearrangement of nuclei coincides with a suitable intersystem crossing.

Table 1. Experimental Energy Decomposition Analysis and Reaction Classification of Selected Two-Electron Systems[a]

reaction:	n (e)	ΔE (eV)	$\Delta E/n$ (eV e^{-1})	$\Delta\bar{\chi}$ (eV e^{-1}), (%)[c]	$\Delta V_{NN}/n$ (eV e^{-1})	$\Delta\omega/n$ (eV e^{-1})	classification:
$2H \rightarrow H_2$, $d_{exp} = 0.741$ Å	2	−4.792[b]	−2.396	−1.828 (76)	9.716	−10.285	nuclear-resisted
$H + e^- \rightarrow H^-$[a]	2	−0.754	−0.377	6.045 (48)	0.000	−6.422	multielectron-favored
$H_2 \rightarrow H_2^+ + e^-$, $d_{exp} = 1.052$ Å	2	15.739	7.870	0.457 (6)	−2.872	10.285	nuclear-favored
$He \rightarrow He^+ + e^-$[a]	2	24.587	12.293	2.621 (21)	0.000	9.672	deformation

[a]Experimental data from the NIST Chemistry WebBook. [b]$\Delta E \approx \Delta H^0 - E_{ZPE}$, where $E_{ZPE} = 1/2h\sum_i {}^c\nu_i {}^c\Delta\chi$ contribution according to eq 13. The examples shown here are simple. We ensure the reader that we will broach complexity and chemical utility in subsequent papers.

The four classes of reactions in which electronegativity, the average binding energy, can be used as a reliable predictor of exoergic preference are as follows: relaxation, binding-favored, nuclear-resisted, and multielectron-resisted. For the remaining four cases electronegativity arguments will predict an energy trend opposite to what is actually observed. With this approach one can start out by rationalizing a reaction course with Pauling electronegativity (or any other scale, including our average binding energy) and then easily check after the fact with this analysis if that rationalization is reasonable, or explain why there is no correlation. In the latter situations we now know where to turn, ΔV_{NN} and $\Delta \omega$.

TOWARD EXPERIMENTAL QUANTUM CHEMISTRY

The energy decomposition introduced in eq 2 is a way of attaining explicit knowledge of molecular multielectron interactions, obtained from experimental data. From this perspective, and because of a natural complementarity and interchangeability of calculated and experimental data in this analysis, we can, in a way, begin to talk about experimental quantum chemistry.

For all the reactions listed in Table 1, each has zero multielectron interactions on one side of the reaction arrows (H, He$^+$, and H$_2^+$ have only one electron each). In other words, H$_2$, H$^-$, and He ionization effectively removes all electron–electron interactions. The same is true for the dissociation of molecular hydrogen. Therefore, the experimental $\Delta \omega / n$ energies in Table 1 are absolute measures of the multielectron interactions in H$_2$, H$^-$, and He.

The multielectron interactions decrease as H$_2$ (10.285 eV e^{-1}) < He (9.672 eV e^{-1}) < H$^-$ (6.422 eV e^{-1}). The largest magnitude of ω is observed in H$_2$, because in this situation electrons are required to concentrate in-between the two protons, to offset their nuclear repulsion. This effect can be judged by comparing to the spherically symmetric helium atom, which has an ω value 94% that of molecular hydrogen. Finally, the hydride anion has electrons distributed more diffusely, which naturally results in a lower ω value, 62% that of molecular hydrogen.

This approach highlights several tantalizing prospects. For instance, given that we begin with a one-electron system for which we know the absolute energy, such as C^{5+} (-489.993 eV), it should, in principle, be possible to estimate the absolute energy of any subsequent larger multielectron system, like the carbon atom, or molecules derived thereof, by a series of relative measures. This assumes that we can measure accurate adiabatic electron attachment energies (electron affinities), or ΔE, for each necessary step. Photoelectron spectroscopy of each intermediate would reveal $\bar{\chi}$, which, in combination with the estimated total energy, enables extraction of ω. If multiple nuclei are involved then structure determinations are needed to measure ΔV_{NN}, which accounts for geometry relaxation.

The technical difficulties of an undertaking aimed at absolute energies will certainly be substantial. Fortunately, what matters most in chemistry and physics are relative measures. As we have described, the implementation of the $\Delta \bar{\chi}$-based energy decomposition analysis enables quantitative comparisons over and between any two transformations.

CONCLUSIONS

Even with today's great advances in computational chemistry the concept of electronegativity remains a proven, useful tool. It

is of particular importance when chemistry is to be quickly and "intuitively" rationalized. Building on Lee Allen's definition of configuration energies, this work begins by relating the classical notion of electronegativity to the average electron binding energy. This quantity, denoted $\bar{\chi}$, is an average property obtainable for any system with discrete electronic levels, such as atoms and molecules, or with continuous bands, such as in condensed matter. The average binding energy is, in principle, accessible from experiment, through photoelectron and X-ray spectroscopy. There are multiple approaches of approximating $\bar{\chi}$ theoretically, ranging from single and multireference wave mechanics and DFT.

Molecular orbital theory has taught us the great predictive power of orbitals. Can $\bar{\chi}$ lead us to more chemistry still? The average binding energy, $\bar{\chi}$, has a rigorous, and understandable, connection to the total energy. But $\bar{\chi}$ is not the only thing that changes in a chemical reaction or geometry change in a molecule. There are in fact three primary contributions to the changing total energy: the average electron binding energy $\Delta \bar{\chi}$, the nuclear–nuclear repulsion ΔV_{NN}, and multielectron interactions $\Delta \omega$. $\Delta \bar{\chi}$, ΔV_{NN}, and $\Delta \omega$ define a new energy partitioning. We can classify all chemical and physical transformations into four main types (Table 2), which describe whether a transformation is energetically favored or resisted by the collective changes to the binding energy of electrons, the movement of nuclei, or multielectron interactions. In doing so we gain insight into the predominant factors behind a particular energetic preference. For instance, in H$_2$ formation $\Delta \bar{\chi}$ outweighs ΔV_{NN} and $\Delta \omega$, but in electron attachment to H, $\Delta \omega$ dominates. The balance of $\bar{\chi}$, ΔV_{NN}, and $\Delta \omega$ can also be used to predict when more traditional electronegativity arguments can be justifiably invoked in the rationalization of a particular event. In the next paper in this series, we will study bond formation in a wide range of diatomics.

In a time of ever increasing interdisciplinary research, we believe that both $\bar{\chi}$ and the $\bar{\chi}$-based energy decomposition analysis, presented herein, can be quick and reliable tools for those seeking to understand the collective "will" of orbitals and bands and chemistry and physical transformations.

METHODOLOGY

All experimental data are taken from the National Institute of Standards and Technology (NIST) WebBook, unless otherwise specified. All energies are given in electronvolt (eV) or electronvolt per electron (eV e^{-1}) units. One eV = 96.4853 kJ/mol = 23.0605 kcal/mol. To approximate the electronic energy of formation ΔE_f from experimental heats of formation, ΔH_f^0, and vibrational spectroscopy, the experimental harmonic zero-point energy E_{ZPE} is subtracted, i.e. $\Delta E \approx \Delta H^0 - E_{ZPE}$, where $E_{ZPE} \approx 1/2 h \sum \nu_i$, and where ν_i is the ith fundamental frequency of the molecule.

Experimental geometries were used throughout, except for the molecular fragments shown in Figure 2. These geometries were obtained by optimization at the M06-2X[80−82]/cc-pwCVTZ level of theory, using Gaussian 09.[83]

The absolute values of calculated $\bar{\chi}$'s are dependent on the basis set. In particular diffuse functions are crucial (see the Supporting Information). Here all calculated $\bar{\chi}$ values have been approximated from molecular orbital energies, following all-electron calculations using the range-separated LC-BLYP[52] functional, together with the aug-cc-pVQZ basis set.

Whereas valence states can be obtained with a high accuracy with modern range-separated DFT functionals,[84,85] the orbital energies of core electrons are unfortunately underestimated. It has been proposed that the DFT self-interaction error is to blame. One solution is the use of functionals that include pseudospectral regional self-interaction

correction.[84] However, as such methodologies are still in their infancy and exhibit poor general accuracy, we have not applied them at this time. A popular approach to calculating core electron binding energies is referred to as ΔSCF (SCF = self-consistent field). It requires the explicit converging of ground and core-ionized state densities and taking their energy difference.[86] Yet another computational possibility is to combine the results of a suitable level of theory, with experimental reference energies, obtained from X-ray photoelectron spectroscopy, X-ray absorption, X-ray emission spectroscopy, or other related techniques.

Contrary to the absolute values of $\bar{\chi}$, estimations of $\Delta\bar{\chi}$ are considerably more reliable, because of error cancellations. This is true irrespective of whether $\bar{\chi}$'s are estimated theoretically or measured experimentally. Calculations of $\Delta\bar{\chi}$ appear only marginally affected by basis set deficiencies. Similarly, whereas the absolute $\bar{\chi}$ values can vary quite significantly between different levels of theory, this is not our experience for $\Delta\bar{\chi}$. All of the reported $\Delta\bar{\chi}$ values, obtained with LC-BLYP, could be closely reproduced by calculations with the M06-2X functional. In principle, the energies of core electrons can shift in the opposite direction to those of the valence band, in which case their exclusion from a calculation, e.g., using pseudopotentials, will cause an error in the relative average binding energies, $\Delta\bar{\chi}$. Nevertheless, for many transformations a valence-only approach should offer an acceptable approximation to $\Delta\bar{\chi}$.

The valence $\bar{\chi}$ of graphene was estimated from periodic plane-wave calculations using the HSE06 hybrid exchange-correlation density functional[87] and the Vienna Ab Initio Software Package. The default projector augmented wave[88,89] potential for carbon and a 600 eV plane wave energy cutoff were implemented. Brillouin zone integration of the primitive unit cell was performed on a Γ-centered grid, which spanned $21 \times 21 \times 1$ k-points. The DOS energy scale was referenced to the true vacuum by analyzing the value of the local potential far from the graphene sheet. See the Supporting Information for further details.

A python script for performing the $\bar{\chi}$-analysis on molecules and atoms is provided in the Supporting Information. It relies on cclib,[90] which can interpret output from numerous popular quantum chemistry programs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05600.

> Demonstration of $\bar{\chi}$ from canonical and localized orbitals. Discussion on how to calculate $\bar{\chi}$ for extended systems. Dependence of $\bar{\chi}$ on the level of theory and basis set. Python code for performing the $\bar{\chi}$-analysis (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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