

Estimation of atomic correlation energies from the electron density at the nucleus and atomic additivity of the correlation energy in molecules

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ABSTRACT

A new method based on electron density at the nucleus is presented to determine electron correlation energy in atomic species. Using the nuclear-electron coalescence cusp condition, we have shown that the atomic correlation energy can be well represented by different power of atomic number for different isoelectronic series. The computed correlation energies have been achieved chemical accuracy with average absolute deviation in the order of 1 kcal/mol for 17 isoelectronic series. Also it is shown that the correlation energy for a molecule can be expressed in terms of the correlation energies of its constituent atoms and its number of electrons. The proposed formula confirms that in a molecule the electron correlation is larger than the sum over electron correlations of its corresponding constituent atoms.

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1. Introduction

The problem of determining electron correlation energy is of great importance in quantum chemistry and solid state physics. The origin of this problem can be traced to the Hartree–Fock approximation. It is an independent electron approximation in which the instantaneous electron–electron repulsion is replaced by an averaged electron–electron interaction in the Hamiltonian. Consequently, the Hartree–Fock ground state has a higher energy than the true ground state and the difference is defined as the correlation energy. This problem was recognized very early in the development of quantum mechanics as applied to atoms and molecules.

Historically, after Wigner's finding [1] that the atomic correlation energy is a function of atomic number, many attempts have been made to evaluate correlation energy contribution from measurable properties in an approximation manner. Clementi [2] estimated correlation energy of atoms by subtracting from the experimental ground state energies obtained from Moore's tabulation [3] the values of the corresponding Hartree–Fock energy and relativistic corrections [4] from Breit–Pauli perturbation theory. That work has been complemented by analysis of the degeneracy effect in the isoelectronic series of the second row atoms [5]. More recently, Clementi and Corongiu [6] obtained equation of the form

$$E_{\text{corr}} = -0.0170N^{1.31}(e^2/a_0) \quad (1)$$

for neutral atoms, where N is a number of electrons and a_0 is the Bohr radius.

Davidson and co-workers have improved the correlation energy of the ground state atomic ions with 3–10 electrons and Z up to 20 by combining experimental data and improved ab-initio calculations [7]. They used experimental estimate of correlation energy contribution to ionization energy to fit the low- Z data for $N = 3$ –5 satisfactorily to a three-term series in Z^{-1} of the form

$$\Delta E_{\text{corr}}(N, Z) = a + b/Z + c/Z^2 \quad (2)$$

This approach was then extended to atomic ions with 11–18 electrons [8].

Alonso and Cordero have noticed that the empirical correlation energy of atoms and singly charged positive and negative ions show a roughly linear dependence with respect to the number of electrons. Thus, they suggested that the correlation energy of atom is proportional to the number of pairing $N_{\uparrow\downarrow}$ between antiparallel-spin electrons in the same main shell [9],

$$E_{\text{corr}} = -\alpha N_{\uparrow\downarrow} \quad (3)$$

where the empirical constant α has the meaning of a general pairing energy. They substantially improved the relation between E_{corr} and $N_{\uparrow\downarrow}$ by considering separate linear relation that is different slope α for different groups of atoms, related to electronic subshell filling [10].

Silva et al. [11] used the backpropagation neural network to estimate the correlation energy of diatomic molecules and neutral atoms up to radon (Rn). The advantage of using the neural network is that the correlation energy of many electron systems can be generated without prohibiting computational implications.

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In the present study, a simple method based on the electron density at the nucleus has been proposed to estimate the electron correlation for atomic species. The additivity scheme has been also used to determine the molecular correlation energy for 35 closed-shell polyatomic molecules composed of H, C, N, O and F atoms.

2. Computational details

Recently, Parr and Liu have shown that the ground state atomic correlation energies can be well represented by empirical formula of the form

$$E_{\text{corr}} = CN\rho(0)Z^{-\gamma} \quad (4)$$

where C and γ are constants, N is the number of electrons and $\rho(0)$ is the electron density at the nucleus [12].

Here, we use the nuclear-electron cusp condition on $\rho(r)$ which results

$$\rho(0) = AZ^B \quad (5)$$

where A and B are determinable parameters [13].

Inserting $\rho(0)$ from Eq. (5) into Eq. (4) and considering the number of electrons as a variable of the order of α , (N^α), the new form of the correlation energy can be written as;

$$E_{\text{corr}} = \lambda N^\alpha Z^\beta \quad (6)$$

where α , β and λ are constants that can be determined within a sets of atomic and ionic species.

To test the proposed formula, we used a set including atoms from He through Ar as well as their singly charged positive ions. Accurate values of correlation energy of the species were taken from Ref. [8] to determine the constants α , β and λ by multiple linear regressions on the following equation which is equivalent to Eq. (6),

$$\ln E_{\text{corr}} = \ln \lambda + \alpha \ln N + \beta \ln Z \quad (7)$$

All over our work, the correlation energies are taken as positive quantities for simplicity.

3. Results and discussion

3.1. Atomic correlation energy

The fitting values for λ , α and β were found to be 0.0133, 1.116 and 0.278, respectively. These fitted parameters were used to calculate the correlation energies for the species included in our data set using the following equation,

$$E_{\text{corr}} = 0.0133 N^{1.116} Z^{0.278} \quad (8)$$

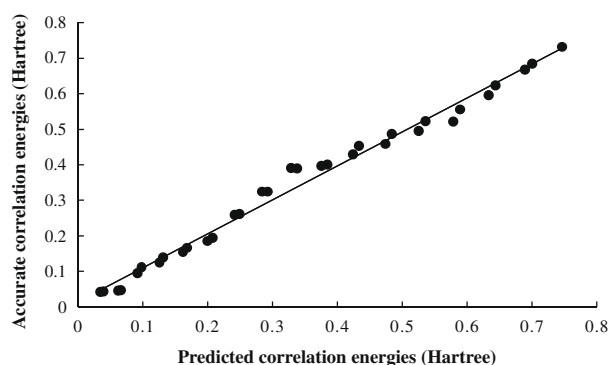


Fig. 1. Accurate versus predicted correlation energies for 33 species including He through Ar as well as their singly charged positive ions.

The accurate values of correlation energies versus the predicted values are shown in Fig. 1 for 33 neutral and charged atoms. Although the regression coefficient $R^2 = 0.983$ indicates a rather satisfactory comparability between our results and the accurate values, the absolute deviations are some times more than 6 kcal/mol which are far from chemical accuracy. This deviation is due to different behavior of the correlation energy in species with different number of electrons.

To approach a higher accuracy we relax the restriction that N is variable and let λ and β to be separately determined for isoelectronic series. Thus, the Eq. (6) can be rewritten as

$$\frac{E_{\text{corr}}}{N} = \lambda Z^\beta \quad (9)$$

We simply do a linear regression fit of the following equation and determine the best values of λ and β for each series with $N = 4-18$

$$\ln \frac{E_{\text{corr}}}{N} = \ln \lambda + \beta \ln Z \quad (10)$$

The computed values for λ , and β , regression coefficients (R^2) and the average absolute deviation (AAD) for 15 isoelectronic series are summarized in Table 1.

In Figs. 2–5 we plot the correlation energy versus atomic number for the ground state of isoelectronic series with $N = 2-18$. The plots confirm again that the correlation energy takes a different power of Z for different isoelectronic series. More specifically, for $N = 7-11$ (Fig. 2) the correlation energies take almost the same trend and β parameters have similar order. This similarity has been also observed for $N = 6, 12-18$ (Fig. 3), where the correlation energies follow a well defined trend. The reported values of λ and β parameters for $N = 4, 5$ show that the correlation energy depends on Z with completely different slope (Fig. 4).

A close look at the deviations reveals that the Eq. (9) is accurate enough for computing the correlation energy in isoelectronic series ($N = 4-18$) and a proper accordance, within chemical accuracy, has been observed between the predicted and accurate correlation energies.

A comparison between Figs. 2–4 and Fig. 5 shows that for isoelectronic series with $N = 2, 3$ the correlation energy is not a linear function of atomic number. However, for $N = 2, 3$ the correlation energies are poorly fitted to the Eq. (10) and the regression coefficients are in the order of 0.690. Therefore, for isoelectronic series with $N = 2, 3$ a quadratic fit of the below form has been used.

$$\ln \frac{E_{\text{corr}}}{N} = \ln \lambda + \beta \ln Z + \gamma (\ln Z)^2 \quad (11)$$

The accurate correlation energies of species with $N = 2, 3$ from Ref. [7] are then used to find the best fit for parameters λ , β and γ . The

Table 1

Fitting parameters, regression coefficients and average absolute deviations (kcal/mol) of Eq. (10) for isoelectronic series with $N = 4-18$.

N	β	λ	R^2	Number of data points	AAD
4	0.736	0.008	0.999	25	1.74
5	0.528	0.011	0.998	24	1.20
6	0.317	0.015	0.999	23	0.49
7	0.116	0.022	0.957	22	1.08
8	0.094	0.027	0.984	21	0.70
9	0.074	0.031	0.992	20	0.54
10	0.052	0.034	0.976	19	0.47
11	0.094	0.029	0.985	18	0.70
12	0.266	0.019	0.996	17	0.95
13	0.318	0.016	0.995	16	1.34
14	0.335	0.015	0.995	15	1.61
15	0.335	0.015	0.997	14	1.06
16	0.357	0.014	0.997	13	1.07
17	0.365	0.014	0.998	12	0.98
18	0.371	0.014	0.999	11	0.90

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