Correlation energies of light atoms related to pairing between antiparallel spin electrons

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Abstract

Early theoretical work emphasized the gross trend of the total correlation energy of neutral atoms with atomic number Z. This was later improved quantitatively, by focusing on the number of pairings between antiparallel-spin electrons in the same main shell (i.e., K, L, M . . . shells). Here, this viewpoint is pressed, and correlation energies associated with s–s, s–p and p–p pairings are extracted. The s–s energy turns out to be rather insensitive to a change from K to L shells, but a small increase is found to occur in the M shell. Also, the s–p and p–p pairing energies show a small increase from the L to the M shells. The s–s and s–p energies are $\approx$1 eV, the s–s contribution being the larger. The p–p energy is $\approx$1/3 eV. The effect of removing or adding one electron to the neutral atom has also been analysed. Wavefunction overlap and wavefunction localization appear to control the values of the pairing energies.

1. Introduction

March and Wind [1] have observed a grossly linear relation between the empirical correlation energies E_c of neutral atoms in their ground state and the atomic number Z (equal to the number of electrons in the neutral atom),

$$-E_c = AZ. \tag{1}$$

That study was restricted to $Z \leqslant 18$, because the empirical correlation energies are difficult to estimate for heavier atoms. Calculations of the correlation energy [2, 3] within the framework of density functional theory (DFT) [4] indicate that the linearity is also approximately valid for larger values of Z. From high dimensionality d extrapolation to $d = 3$, other work predicted [5] that the gross variation of E_c with Z should be proportional to $Z^{4/3}$ for large Z.

However, by looking in detail at the behaviour of the empirical E_c versus Z, Alonso and Cordero [2, 6] have noticed some systematic deviations from the linear trend for open

shell atoms. The alkali atoms are an example: the correlation energy of lithium ($Z = 3$) is very similar to that of helium ($Z = 2$), and the correlation energy of sodium ($Z = 11$) is very similar to that of neon ($Z = 10$). Also, the rate of increase of E_c with Z across a p subshell is not constant, and drastically changes after the p subshell is half filled. Since correlation cancels some of the classical Coulombic interaction (a two-body term) by lowering the probability of two electrons being too closely together in space, one could expect the number of electron pairings to be a relevant variable. In fact, the detailed behaviour of E_c was explained in a previous paper [6] by a model in which the correlation energy is proportional to the number of pairings $N_{\uparrow\downarrow}$ between antiparallel-spin electrons, that is

$$-E_c = \alpha N_{\uparrow\downarrow}. \tag{2}$$

The constant α has the meaning of a general *pairing energy*. In the counting of $N_{\uparrow\downarrow}$ in this model, the pairings are non-exclusive, that is, a given electron can be paired (correlated) to many others, but the pairings are restricted to electrons in the same main shell (K shell, L shell, M shell, ...). That is, intershell correlations are neglected, and their small effect is cast approximately in the empirical constant α.

By going a step forward, in the present paper we show that the relation between E_c and $N_{\uparrow\downarrow}$ becomes substantially improved by considering separate linear relations, that is different slopes α for different groups of atoms, related to electronic subshell filling. This introduces orbital-dependent pairing energies that, in our opinion, help us to understand the nature of the electronic correlations in atoms. Since correlation is an effect of the Coulomb repulsion that prevents two electrons from approaching too closely in the same region of space, we have found that the strength of the correlation is sensitive to the magnitude of the overlap between the single-particle orbitals occupied by those two electrons (low overlap implies less need for correlation), and to the localization of the orbitals.

2. Correlation energies of neutral atoms related to pairing between antiparallel spin electrons

The empirical correlation energy of an atom is usually defined as

$$E_c = E_{exp} - E_{HF} - E_{rel} \tag{3}$$

where E_{exp} is the experimental total energy, calculated by adding the successive measured ionization energies, E_{HF} is the calculated Hartree–Fock energy of the atom and E_{rel} is the relativistic contribution to the total energy. In DFT, the correlation energy can be formally written [7]

$$E_c[\rho_\uparrow, \rho_\downarrow] \cong \frac{1}{2} \sum_{\sigma \neq \sigma'} \int \int \rho_\sigma(r_1) \frac{g^{\sigma\sigma'}(r_1, r_2)}{r_{12}} \rho_{\sigma'}(r_2) \, d^3r_1 \, d^3r_2. \tag{4}$$

Here $r_{12} = |r_1 - r_2|$ is the interelectronic distance and $g^{\sigma\sigma'}(r_1, r_2)$ is the pair-correlation function for Coulomb correlations, averaged over the coupling constant which turns on the electron–electron interaction. The quantity $\rho_{\sigma'}(r_2)g^{\sigma\sigma'}(r_1, r_2)$ is usually interpreted as the Coulomb hole around an electron with spin σ at r_1. This Coulomb hole consists of a displacement of the charge in the close neighbourhood of the reference electron to a region some distance away, induced by the Coulomb repulsion. The important contribution to the Coulomb hole comes from correlations between electrons with antiparallel spins, that is, $\sigma' \neq \sigma$. The Coulomb correlation between parallel spin electrons is, in general, very small for atoms because exchange (Fermi correlation) keeps those electrons apart. In fact, the Coulomb correlation between parallel-spin electrons is often altogether neglected [8, 9], and we have followed this

view in writing equation (4). By constructing the electron spin-density from the occupied Kohn–Sham orbitals

$$\rho_\sigma(\boldsymbol{r}) = \sum_i^{occ} |\varphi_i^\sigma(\boldsymbol{r})|^2 \tag{5}$$

and inserting this decomposition for $\rho_\sigma(\boldsymbol{r}_1)$ and $\rho_{\sigma'}(\boldsymbol{r}_2)$ in equation (4), one arrives at the expression

$$E_c = \tfrac{1}{2} \sum_\sigma \sum_i \sum_j E_{ij}^\sigma \tag{6}$$

with

$$E_{ij}^\sigma = \int \int |\varphi_i^\sigma(\boldsymbol{r}_1)|^2 \frac{g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{r_{12}} |\varphi_j^{\sigma'}(\boldsymbol{r}_2)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2; \qquad (\sigma \neq \sigma'). \tag{7}$$

The sum in expression (6) involves the number $N_{\uparrow\downarrow}$ of antiparallel spin pairs. These pairings are non-exclusive; that is, a given electron can be paired to many others. The function $g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is negative for small r_{12} and positive for large r_{12}. Then $g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)/r_{12}$ can be interpreted as an effective pairing interaction between electrons with antiparallel spins. It decreases the probability of finding two electrons with antiparallel spins at small distance r_{12}, enhancing the probability at large r_{12}. Evidently, the net effect, that is, the value of E_{ij}^σ, is negative, since correlation energies, which are the sum of the E_{ij}^σ contributions, are negative.

Alonso and Cordero [6] argued that the main contribution to E_c for free atoms comes from E_{ij}^σ interactions between electrons in the same main shell (K shell, L shell, etc). This conclusion arises from the analysis of the integrand in equation (7), which involves three factors: one of these is the effective pairing interaction $g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)/r_{12}$ and the other two are the orbital densities $|\varphi_i^\sigma(\boldsymbol{r})|^2$ and $|\varphi_j^{\sigma'}(\boldsymbol{r})|^2$. First, one has to notice that the atomic orbitals decay exponentially, and that orbitals φ_i and φ_j, belonging to different main shells, are located in different regions of space, with little overlap. This is shown in figure 1 for the orbitals of the carbon atom obtained in a DFT calculation using the local density approximation (LDA) for exchange and correlation [10]. The plot shows the good spatial separation between the K shell (1s electrons) and the L shell (2s, 2p electrons), and also that the 2s and 2p orbitals overlap strongly because these are located in the same region of space. On the other hand, the pairing effect (exclusion of mutual presence) is stronger for small interelectronic separation; in this case $|g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)|$ is sizable and r_{12} small, so $|g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)|/r_{12}$ is large. Consequently the double integral in equation (7) is expected to have a sizable value when the two orbitals overlap strongly (that is, when they belong to the same main shell), because in such a case the three factors in the integrand contribute in the same direction. In contrast, little or no overlap leads to negligible values of E_{ij}^σ. By combining equation (7) with the direct Coulomb repulsion between electrons in spin orbitals $\varphi_i^\sigma(\boldsymbol{r})$ and $\varphi_j^{\sigma'}(\boldsymbol{r})$, we can form the quantity

$$\int \int |\varphi_i^\sigma(\boldsymbol{r}_1)|^2 \frac{1 + g^{\sigma\sigma'}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{r_{12}} |\varphi_j^{\sigma'}(\boldsymbol{r}_2)|^2 \, \mathrm{d}^3 r_1 \, \mathrm{d}^3 r_2 \tag{8}$$

with the meaning of a reduced (correlation-corrected) Coulomb repulsion. The additional assumption that all the E_{ij}^σ terms (between antiparallel electrons in the same main shell) have a common constant value, α, leads to the result of Alonso and Cordero [6] given in equation (2) above. The number of antiparallel pairs, $N_{\uparrow\downarrow}$, is given for all atoms up to $Z = 18$ in table 1.

A plot of the empirical correlation energies [11] as a function of $N_{\uparrow\downarrow}$ was given in [6]. The deviations of the points representing each atom from a linear fit to the whole data are small and support the main assumptions of the model: (1) neglect of correlations between electrons with parallel spins; (2) neglect of correlations between electrons in different main shells;
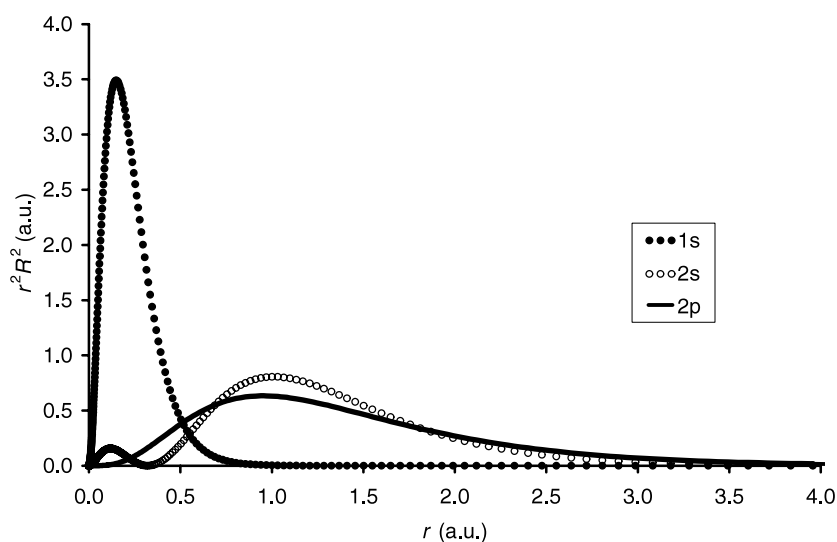
Figure 1. Radial densities $r^2 R^2(r)$ of the 1s, 2s and 2p orbitals of the carbon atom. The densities were obtained from a DFT calculation with the LDA [10] for exchange and correlation. $R(r)$ is the radial part of the wavefunction.

Table 1. Atomic number Z, electronic configuration, number of antiparallel spin pairings and empirical correlation energy [11] in neutral atoms with $Z = 1$–18.

Z	Element	Electronic configuration	$N_{\uparrow\downarrow}$	$-E_c$ (eV)
1	H	$1s^1(\uparrow)$	0	
2	He	$1s^2(\uparrow\downarrow)$	1	1.142
3	Li	He $2s^1(\uparrow)$	1	1.238
4	Be	He $2s^2(\uparrow\downarrow)$	2	2.571
5	B	He $2s^2(\uparrow\downarrow)2p^1(\uparrow)$	3	3.041
6	C	He $2s^2(\uparrow\downarrow)2p^2(\uparrow\uparrow)$	4	4.258
7	N	He $2s^2(\uparrow\downarrow)2p^3(\uparrow\uparrow\uparrow)$	5	5.129
8	O	He $2s^2(\uparrow\downarrow)2p^4(\uparrow\uparrow\uparrow\downarrow)$	9	7.020
9	F	He $2s^2(\uparrow\downarrow)2p^5(\uparrow\uparrow\uparrow\downarrow\downarrow)$	13	8.761
10	Ne	He $2s^2(\uparrow\downarrow)2p^6(\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow)$	17	10.612
11	Na	Ne $3s^1(\uparrow)$	17	10.816
12	Mg	Ne $3s^2(\uparrow\downarrow)$	18	12.068
13	Al	Ne $3s^2(\uparrow\downarrow)3p^1(\uparrow)$	19	13.061
14	Si	Ne $3s^2(\uparrow\downarrow)3p^2(\uparrow\uparrow)$	20	14.163
15	P	Ne $3s^2(\uparrow\downarrow)3p^3(\uparrow\uparrow\uparrow)$	21	15.061
16	S	Ne $3s^2(\uparrow\downarrow)3p^4(\uparrow\uparrow\uparrow\downarrow)$	25	17.265
17	Cl	Ne $3s^2(\uparrow\downarrow)3p^5(\uparrow\uparrow\uparrow\downarrow\downarrow)$	29	19.442
18	Ar	Ne $3s^2(\uparrow\downarrow)3p^6(\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow)$	33	21.414

(3) approximate constancy of E_{ij}. However, a deeper analysis of the data shows clear trends in the small deviations. The empirical correlation energies are plotted in figure 2, this time showing that different linear functions fit accurately separate portions of the data.

Let us first consider the set formed by He, Li and Be. The antiparallel spin pairings involve only s electrons: $(1s\uparrow 1s\downarrow)$ in the K shell for He and Li, and $(1s\uparrow 1s\downarrow; 2s\uparrow 2s\downarrow)$ in the K and L shells for Be. The linearity of $E_c(N_{\uparrow\downarrow})$ for this group of atoms indicates that E_{1s1s} and E_{2s2s}
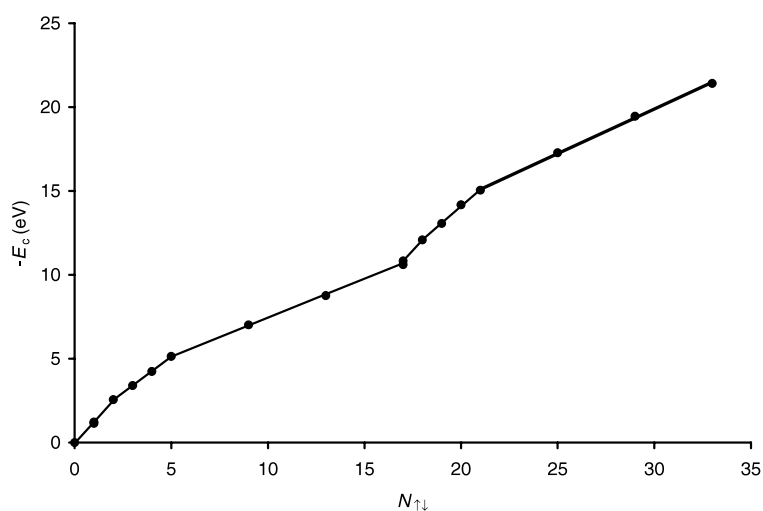
Figure 2. Empirical correlation energies of neutral atoms [11] versus the number $N_{\uparrow\downarrow}$ of antiparallel spin pairings. Both quantities are given in table 1. The plot shows that linear functions restricted to different groups provide a more accurate fit than a single linear fitting for the whole data set.

are approximately the same, and that its value can be estimated as

$$E_c(\text{Be}) = 2E_{\text{ss}}, \tag{9}$$

which gives $E_{\text{ss}} = -1.28$ eV. The slope of the curve $E_c(N_{\uparrow\downarrow})$ changes for the set Be, B, C and N. The new ingredient is the opening of the 2s2p correlation channel for B, C and N. There are one, two and three $2s\downarrow 2p\uparrow$ pairings for B, C and N, respectively, so the correlation energies of those three atoms can be written

$$E_c = E_c(\text{Be}) + nE_{\text{sp}} \tag{10}$$

with $n = 1, 2$ and 3 for B, C and N respectively. We have taken into account Hund's rule, therefore no $2p\uparrow 2p\downarrow$ pairing is present [11]. Using the empirical correlation energy of nitrogen in equation (10), one obtains $E_{\text{sp}} = -0.86$ eV. A new set is composed of the elements N, O, F and Ne. With four, five and six electrons in the 2p subshell for O, F and Ne, respectively, an increased number of sp pairings is formed, this time $2s\uparrow 2p\downarrow$ pairings, but, since the 2p subshell is now more than half filled, $2p\uparrow 2p\downarrow$ pairings also appear. For instance, for the closed shell atom Ne, E_c can be written

$$E_c(\text{Ne}) = E_c(\text{N}) + 3E_{\text{sp}} + 9E_{\text{pp}} \tag{11}$$

or, in the equivalent form,

$$E_c(\text{Ne}) = E_c(\text{Be}) + 6E_{\text{sp}} + 9E_{\text{pp}}. \tag{12}$$

This leads to $E_{\text{pp}} = -0.32$ eV. In conclusion, orbital-dependent pairing energies E_{ss}, E_{sp} and E_{pp} allow for an accurate description of the total correlation energies of low Z neutral atoms with electrons in the K and L shells.

Confirmation of the idea of orbital-dependent pairing energies is provided by the analysis of the period Na–Ar, which parallels the shell filling behaviour of the previous period. For instance,

$$E_c(\text{Mg}) = E_c(\text{Ar}) + E_{3s3s} \tag{13}$$

Table 2. Orbital-dependent pairing energies (eV) between electrons with antiparallel spins.

	E_{ss}	E_{ss}	E_{sp}	E_{sp}	E_{pp}	E_{pp}
Shell	K, L	M	L	M	L	M
Cations	−1.51	−1.93	−0.75	−0.75	−0.35	−0.50
Neutrals	−1.28	−1.44	−0.86	−1.00	−0.32	−0.37
Anions	−0.99	−0.67	−1.00	−1.04	−0.31	−0.31

allows one to estimate $E_{ss} = -1.44$ eV, in reasonable agreement with the value $E_{ss} = -1.28$ eV obtained from 1s1s and 2s2s pairings. In a similar way, consideration of the set Al, Si and P introduces 3s3p correlations, and finally the set S, Cl and Ar brings in 3p3p correlations. The pairing energies estimated by the same analysis are $E_{sp} = -1.00$ eV and $E_{pp} = -0.37$ eV. The agreement with the corresponding pairing energies for the K and L shells is satisfactory and supports the idea of ss, sp and pp correlations nearly independent of the main shell (although, of course, restricted to electrons in the same main shell). All the calculated pairing energies are collected in table 2.

The relative magnitude of the calculated pairing energies follows the ordering

$$-E_{ss} > -E_{sp} > -E_{pp}. \qquad (14)$$

This appears to be due to two effects. The first one is the degree of overlap between the two orbitals involved. $g^{\sigma\sigma'}(r_1, r_2)/r_{12}$ in equation (7) is independent of the orbital angular momentum character of the two electrons correlated, so the magnitude of E_{ij}^{σ} depends on the strength of the spatial overlap between $\varphi_i^{\sigma}(r)$ and $\varphi_j^{\sigma'}(r)$. Coulomb repulsion has the effect of decreasing the probability of two electrons being near to each other, and this decrease is embodied in the so called *correlation hole*, the quantity $[\rho_{\sigma'}(r_2)g^{\sigma\sigma'}(r_1, r_2)]$ in equation (4). The wavefunctions $\varphi_s^{\uparrow}(r)$ and $\varphi_s^{\downarrow}(r)$ for two s electrons in the same main shell are essentially identical, so their overlap is maximum and correlation acts at full strength to reduce their repulsion. The overlap between $\varphi_{ns}^{\uparrow}(r)$ and $\varphi_{np}^{\downarrow}(r)$ is still substantial (see the 2s and 2p orbitals of carbon in figure 1), but lower than the overlap between two s electrons. In particular, one can notice that the positions of the main maxima of the radial probability density of $\varphi_{2s}(r)$ and $\varphi_{2p}(r)$ do not coincide. Their relative positions require less correlation, and consequently $-E_{sp}$ is smaller than $-E_{ss}$. The p electrons have three orbitals available, p_x, p_y and p_z, pointing towards mutually perpendicular directions in space, so wavefunction overlap between antiparallel-spin electrons in different p orbitals is rather small and there is little need to further correlate their relative positions (in comparison with other cases). This accounts in part for the low values of $-E_{pp}$. Of course, overlap between $\varphi_{p_x}^{\uparrow}(r)$ and $\varphi_{p_x}^{\downarrow}(r)$, for instance, is strong; so the values of E_{pp} given in the table come as an average of large and small contributions, the latter dominating because their number is higher. The second effect influencing the relative ordering of the pairing energies is the radial localization of the orbitals. Looking again at figure 1 one can observe that the 2p orbitals are more extended (less localized) than the 2s orbitals, and that the maximum value of the probability $|\varphi_{2p}(r)|^2$ is lower than the maximum of $|\varphi_{2s}(r)|^2$. This fact contributes to the result $-E_{pp} < -E_{ss}$.

It is remarkable that DFT calculations reproduce rather well the detailed behaviour of the correlation energies. Figure 3 shows a comparison of the empirical correlation energies and those calculated by Lagowsky and Vosko [11] by using the gradient corrected correlation energy functional of Perdew [12]. The behaviour of the calculated correlation energy is again piecewise linear and the slopes in the different regions are also rather similar to the empirical ones. However, one can notice a clear failure for the alkali atoms Li and Na. For the two atoms Ne and Na, $N_{\uparrow\downarrow}$ is equal to 17, and consequently their empirical correlation energies are
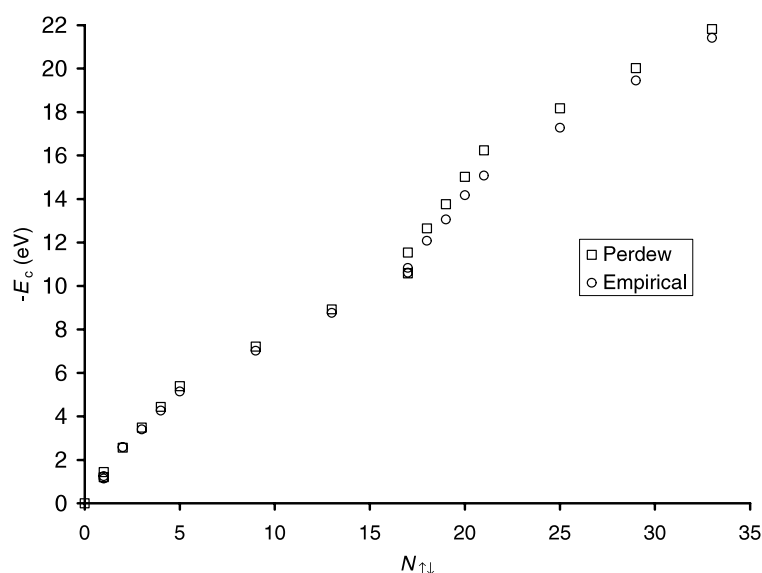
Figure 3. Comparison of the empirical correlation energies of neutral atoms with those obtained by DFT calculations [11] using a gradient-corrected functional of Perdew [12].

extremely close, -10.61 and -10.82 eV, respectively. The DFT calculation gives a correlation energy of -10.59 eV for Ne, which is very close to the empirical one. However, the prediction for Na is -11.53 eV, which, instead of being close to the correlation energy of Ne, is halfway between the DFT values of Ne and Mg. A similar failure occurs for Li, but it is quantitatively less important.

3. Extension to charged atomic ions

Empirical correlation energies have also been estimated [11] for singly charged cations and anions with Z up to 18. Figure 4 shows a combined plot of E_c versus $N_{\uparrow\downarrow}$ for neutral atoms, cations and anions. The behaviour is very similar, independently of the charge state, but, of course, the values of the slopes of the different linear fits are not identical. Table 2 gives the fitted values of E_{ss}, E_{sp} and E_{pp}. The relative ordering of pairing energies given in (14) is also valid for cations. The main differences between neutral atoms and cations occur for E_{ss}. There is an increase of $-E_{ss}$ for cations, which can be ascribed to the increased localization of the wavefunctions of s electrons due to the decreased screening of the nuclear charge. This affects the s electrons most because only those electrons have a substantial probability of presence near the nucleus. The same effect explains the decreased value of $-E_{ss}$ for anions, the over-screening of the nuclear charge being the responsible factor in this case.

The variation observed in the values of E_{sp} is opposite to that discussed for E_{ss}. The changes of s-wavefunction localization with net charge also seem to be responsible for the variation observed in the values E_{sp}. This variation is not large but the trend is for $-E_{sp}$ to decrease with increasing s localization. We can argue that increasing s localization lowers the overlap between $\varphi_{ns}^{\uparrow}(r)$ and $\varphi_{np}^{\downarrow}(r)$ wavefunctions, while decreasing s localization increases that overlap.
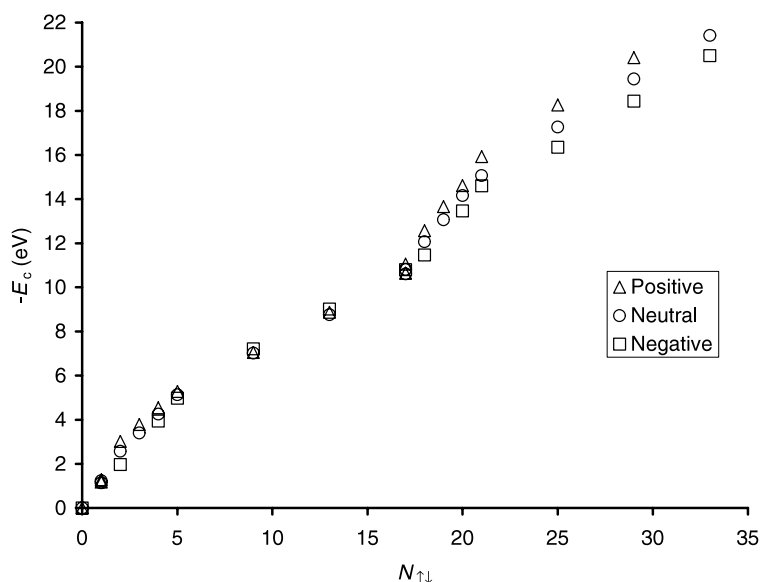
Figure 4. Empirical correlation energies of neutral atoms and singly charged cations and anions versus the number $N_{\uparrow\downarrow}$ of antiparallel spin pairings.

4. Discussion

As emphasized in [1] and [2], the gross independent variable on which the correlation energy of both neutral atoms and atomic ions depends is the total number of electrons. On the other hand, the work of Alonso and Cordero [6] introduced the variable $N_{\uparrow\downarrow}$, the number of pairings between electrons in the same main shell. Therefore, we now assess the relation between those two models, as well as their relation to the more quantitative description of correlation energies presented in this paper.

Starting with the linear relation between $-E_c$ and atomic number given by equation (1), and using table 1 in the modelling of the neutral atom correlation energy as a function of $N_{\uparrow\downarrow}$, we find the slopes of the straight lines analogous to figure 2 as follows: slope of magnitude A from Be to N, slope $A/4$ from N to Ne, slope A from Mg to P and slope $A/4$ from P to Ar. By fixing A to make the empirical correlation energy coincide with the model correlation energy (from equation (1)) for the Ar atom, the value $A = 1.190$ eV (or $A/4 = 0.2975$ eV) is obtained. Using this value of A, the model correlation energies have been plotted in figure 5 as a function of $N_{\uparrow\downarrow}$. The model evidently predicts parallel lines for the regions N–Ne and P–Ar, with slopes $A/4$. The other portions apparent in figure 2 also have equal slopes in the model, but now equal to A. This confirms that the structure of the straight lines in figure 2 comes dominantly from the linearity of the correlation energy with Z, plus the shell structure reflected directly in table 1 by comparing Z and $N_{\uparrow\downarrow}$. Clearly, $N_{\uparrow\downarrow}$ passing from N to Ne has an interval of 4, from Na to P an interval of unity and from P to Ar an interval of 4. This explains the changes of slopes occurring in figure 2.

The real slopes from Be to N, and from Mg to P, obtained from the empirical correlation energies in figure 2 are 0.853 and 0.998 eV respectively. The slopes from N to Ne and from P to Ar, calculated in the same way, are 0.457 and 0.529 eV. These slopes are approximately in the ratio 1 to 1/2, and not in the ratio 1 to 1/4 predicted by the simple model of equation (1). In addition, the model of equation (1) fails in the regions He–Li and Ne–Na. This means that the
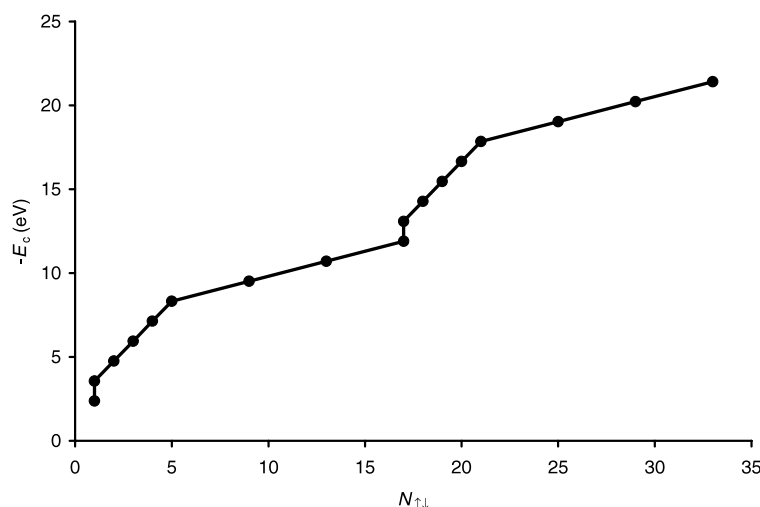
Figure 5. Model correlation energy of neutral atoms, calculated from equation (1), versus the number, $N_{\uparrow\downarrow}$, of antiparallel spin pairings. The slope A in equation (1) was obtained by fitting the correlation energy of Ar.

variation of the correlation energy with Z is only grossly described by a simple one-parameter model, and that a fully quantitative description of E_c needs the orbital-dependent pairing energies of table 2. Using relations (10) and (11), and requiring that the slopes obtained from the orbital pairing energies are in the ratio 1 to 1/4, it is easy to show that the simple model of equation (1) is equivalent to assuming $E_{ss} = E_{sp}$, independent of the main shell, and $E_{pp} = 0$, for neutral atoms. Grossly, this is a zeroth order approximation to the results in table 2. The six orbital-dependent pairing energies of table 2 (for neutral atoms) can be classified into two groups with magnitudes ≈ 1 and $\approx 1/3$ eV, respectively, the latter comprising $-E_{pp}$, and which would be identically zero if the one-parameter model reflected E_c fully quantitatively. Let us also stress that, in the present notation, the model given in equation (2), postulating the linearity between $-E_c$ and $N_{\uparrow\downarrow}$, is equivalent to the approximation of equal pairing energies $E_{ss} = E_{sp} = E_{pp}$. The two models of equations (1) and (2) are then not equivalent and can be viewed as representing two different approximations to the more correct description of correlation energies given in the present paper.

The numerical results obtained for the electronic correlations appear to be intimately related to the fact that the systems studied are isolated atoms (or ions). But it is likely that some of the qualitative ideas arising from the analysis, namely (a) the dominant effect of correlations between electrons in the same main shell, (b) the relevance of wavefunction overlap and (c) the effect of wavefunction localization, are more general and may have application to other many-body systems. We briefly comment on several implications for related systems. The first one concerns condensed matter. The shell (a) and overlap (b) effects are consistent with the core–valence separation commonly used in calculations for metals and other solids, where the atomic core is replaced by a pseudopotential. Underlying this separation scheme is the assumption that core–valence correlations are much smaller than the correlations between valence electrons. Our second example is the Hooke atom, and in particular the two-electron Hooke atom [13], in which the two Coulombically repelling electrons are harmonically confined. An estimation of the correlation energy for the spin-compensated ground state of this artificial atom gives $-E_c \approx 0.79$ eV, which has to be compared with the value $E_c(\text{He}) = 1.14$ eV given in table 1,

or with the pairing energy $-E_{\mathrm{ss}} = 1.28$ eV given in table 2. Actually, the Hookean atom value is closer to the magnitude of E_{ss} for anions in table 2, and this fact reflects the weaker localization of the 1s electrons in the parabolic confinement of the Hookean atom, in comparison to the strongest confinement induced by the nuclear Coulomb potential of the real He atom.

A third example is the so-called pseudoatom model by Moshinsky and co-workers [14]. In this model both the electron–nucleus and electron–electron interactions are replaced by harmonic oscillator interactions (attractive in the first case and repulsive in the second). In this case there is no point in comparing the numerical values of the correlation energies of the pseudoatoms with those of the real atoms. But other properties could be less sensitive to the precise form of the interaction, like the variation of E_c with Z. This is given for singly charged cations with closed electronic shells in figure 6 of [14] and, indeed, the relation between E_c and Z is again roughly linear, as for real atoms, so this seems to be a robust property. We have not investigated the behaviour of E_c between shell closings, since the pseudoatom model was not solved for incomplete electronic shells.

5. Summary and conclusions

The empirical correlation energy of atoms and singly charged positive and negative ions in their ground state shows a roughly linear dependence with respect to the number of electrons. However, the deviations from this linear behaviour, only known precisely for $Z \leqslant 18$, follow a well defined trend. A formulation based on DFT indicates that the correlation energy shows a piecewise linear behaviour as a function of the number $N_{\uparrow\downarrow}$ of pairings between antiparallel spin electrons in the same main shell (K, L, M . . . shells). The slope of that linear relation is different for different groups of atoms, and this allows us to estimate orbital-dependent pairing energies E_{ss}, E_{sp} and E_{pp}, given in table 2. The relative values of those pairing energies can be understood as a consequence of (i) the degree of overlap between the orbitals of the two electrons, and (ii) the localization of those orbitals.

For the future, it would be of interest, when more accurate correlation energies become available for Z higher than 18, to extend the present analysis, even though we recognize that additional pairing energies may have to be introduced. Exploring correlations between electrons in molecules may also provide additional insight.

Acknowledgments

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