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Stability of Doubly-Charged Negative Ions of Atoms in the Density-Functional Theory

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A Watson sphere removed to infinity is used to calculate, doubly charged negative ions of the atoms B, C, N, O, Al, Si, P, and S by the electron-correlation and self-interaction corrected generalized exchange local-spin-density functional theory. These second electron affinities are compared to other theoretical calculations and show the doubly charged negative ions of these atoms to be unstable even when the Watson sphere radius is made infinite by an algebraic equation, but less unstable than in ionic crystals.

1. INTRODUCTION

The stability of negative ions of atoms has attracted attention[1-15]. The existence of doubly charged negative ions[11], such as, O^{2-}, Tc^{2-}, Bi^{2-}, F^{2-}, Cl^{2-}, Br^{2-}, and I^{2-} was found experimentally. Theoretically the stability of doubly charged negative ions of atoms has given rise to some interesting problems. Baughan[16] calculated the first, second, and third electron affinities for atoms using the lattice-energy data of ionic crystals, and spectroscopic data for the corresponding molecules, and estimated the second electron affinities for the elements O, S, and Se and the third electron affinity for N by extrapolation, starting from the first, second and third ionization potentials of the corresponding atom such extrapolations are often unreliable. Gaspar and Csavinsky[17] presented O^{2-}; Watson[18] published O^{2-} results in the Hartree-Fock (HF) theory with an artificial positively charged sphere surrounding the doubly charged negative ion.

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Clementi and McLean[19] reported N^{2-} and O^{2-} and concluded that they were unstable because the second electron affinities were –0.454 Ry for N and –0.444 Ry for O in the electron-correlation corrected HF theory. Ahlrichs[20] pointed out that the HF calculations which yield $\varepsilon_i > 0$ for an occupied orbital do not minimize the HF energy, and calculated some multiply charged negative ions, O^{2-}, N^{3-}, C^{4-}, S^{2-}, $O_2{}^{2-}$, and $C_2{}^{2-}$ in the HF theory by an appropriate admixture of a continuum function to the corresponding orbital, but could not find any evidence of stable multiply charged negative ions, but obtained much lower total energies than Robb and Csizmadia[21]. Kalcher[22] studied the stability of the doubly charged negative ions of Si, P, S, and Cl in a configuration-interaction (CI) calculation, systematically using different substitutions from any configuration of the reference wave functions. He reported that the doubly charged negative ions of Si, P, S, and Cl were unstable with negative electron affinities between –0.0494 Ry and –0.0612 Ry.

There is no successful calculation of doubly charged negative ions of atoms in the gas phase by the local-density functional (LDF) theory[23,24] in the literature, although the LDF theory has been widely used to study molecular bonding, magnetism, cohesion, the surface electronic properties of metals, and semiconductors[25] and to predict the stability of singly charged negative ions[6,7,26-28], because of a non-convergent solution to the one-electron Schrödinger equation with a positive asymptotic potential, as r approaches infinity, in the numerical self-constituent-field (SCF) procedure in LDF theory[29,30]. Cole and Perdew[31] tried to calculate O^{2-} and Te^{2-} in the SIC-LSD theory, but failed to give self-consistent bound solutions.

Second electron affinities of atoms are essential to calculate molecular properties[30], such as the hardness of acids, bases, and atomic groups[32,33], in the quantum-mechanical cluster calculations of defects in ionic solids[34-36], and in calculating the EA(n) in an chemical compound[5], in super halogens MX_{k+1}[38] to calculate the highest electron affinity[39] possible in a molecule and the interatomic distances in ionic solids[30]. Hence the investigation of the stability of the double negative charged ions of atoms is important.

In this work, the self-interaction corrected, generalized exchange local-spin-density functional (SIC-GX-LSD) theory[40], with the Vosko, Wilk and Nusair[41] (VWN) electron-correlation energy functional, is employed to investigate the stability of the doubly charged negative ions of the second and third period elements which involve one orbital in going from the neutral atom to their doubly charged negative ions. As mentioned previously[30], no bound solution can be found by directly solving the Schrödinger equation in the SIC-LSD theory for doubly negative ions. Consequently, a positively charged artificial sphere, proposed by Watson[18] (the Watson sphere) used in molecular anion calculations[41-43], is used to surround the doubly charged negative ion and ensure that the one-electron Schrödinger equation has a bound solution. Obviously, the statistical total energy and the electron-density distribution of a doubly charged negative ion depend on the Watson sphere size r_{WS} and charge $+q$. However, if the charge on the Watson sphere is fixed, and the radius of the Watson sphere is fixed, and the radius of the Watson sphere is gradually increased to infinity, the calculated statistical total energy and the electron-density distribution of the doubly charged negative ion will gradually approach the real statistical total energy and the electron-density distribution of the real doubly charged negative ion. The VWN correlation corrected SIC-GX-LSD theory has been previously established as reliable in predicting the ionization potentials and electron affinities of atoms[6,7,28] compared to experiment, when the Gopinathan, Whitehead and Bogdanović[42] (GWB) Fermi-hole parameters are used. The calculation method is in Refs. 28 and 40.

COMPUTATIONAL DETAILS

The SCF procedure in the electron-correlation corrected SIC-GX-LSD theory was achieved easily for doubly charged negative ions of the elements in the second and third periods with a small Watson sphere ($r_{WS} < 10\ a_0$), whereas it was increasingly difficult when the Watson sphere radius increased. The electronic structures of these doubly charged negative ions are very sensitive to the potential with a large Watson sphere: no converged results were obtained by starting with the converged potential of the neutral atom from a Herman and Skillman calculation[29] and the electron configuration for the corresponding doubly charge negative ions, when the Watson sphere radii are bigger than 10 a_0. Hence, an adiabatic convergence technique[7] was used: starting with the converged potential and electron configuration of the neutral atom, 1 percent of an electron was added in each following iteration until a total of two electrons was included in the extra orbitals. This is possible because the second and third period neutral atoms are very stable systems. This slow, adiabatic change from the neutral atom allows the system to remain in its ground state. The mixture factor was chosen to be 0.01 to 0.001 when the Watson sphere radii increase from 10 a_0 to 62 a_0, the largest Watson sphere radius used in this work, for B^{2-} and Al^{2-}, 10 a_0 to 74 a_0 for C^{2-}, 10 a_0 to 60 a_0 for Si^{2-}, 10 a_0 to 70 a_0 for N^{2-} and P^{2-}, and 10 a_0 to 36 a_0 for O^{2-} and S^{2-}. This means that 99.9 percent of the electron density from the $(i-1)^{th}$ iteration and 0.1 percent of electron density from the i^{th} iteration are combined together to produce the new potential for the $(i+1)^{th}$ iteration, when the mixture factor is 0.001. The SCF procedure was completed when the differences in the wave functions of electrons between the i^{th} and the $(i+1)^{th}$ iterations were less than 10^{-8} at all mesh points. Obviously, the speed of convergence is very slow, and decreases, when the Watson sphere radius increases. In all this work, the net charge on the Watson sphere is +1 e. When the Watson sphere radius is bigger than the largest Watson sphere radius of the corresponding doubly charged negative ions, no converged results were obtained. The largest Watson sphere radius which can be used to produce the converged electronic structure of the corresponding doubly charged negative ion differs for different doubly charged negative ions and depends on the electronic structure and electron configuration. For example, the largest radius is 62 a_0 for both B^{2-} and Al^{2-}, which have the same valence electron configurations with a half occupied p orbital $p_\uparrow^3$.

RESULTS AND DISCUSSION

The additional potential produced by introducing a Watson sphere in the doubly charged negative ions is

$$V_{WS}(r) = \begin{cases} -2/r_{WS}, & \text{when } r < r_{WS} \\ -2/r, & \text{when } r \geq r_{WS} \end{cases} \tag{1}$$

in Rydberg atomic units. The total potential including the Coulomb interactions between the nucleus and electron, electron and electron, and positive charge on the Watson sphere and electron, the exchange and correlation potentials, is certainly a continuous function of the radial *r*. But its derivative is not a continuous function of *r*, because of the Watson sphere potential. The left-hand derivative of the Watson sphere potentials $V_{WS}(r)$, is zero and its right-hand derivative is $2/r^2_{WS}$ at $r = r_{WS}$. Figure 1 plots the product of the potential and the radial *r* for the outermost orbital, $2p\downarrow$, of the doubly charged negative ion of carbon, C^{2-}, against the modified radial *x* (the modified radial *x* is related to the ordinary radial r by $r = 1/2(3\pi/4)^{2/3} Z^{-1/3}x$ with atomic number *Z*) and demonstrates the discontinuous behaviour of the first derivative of the total potential at $r = r_{WS}$. It is very interesting that there is a total potential barrier with positive total potential inside the Watson sphere. The total potential of the outermost orbital gradually increases passing $rV(r) = 0$ with a zero total potential and then becomes positive arriving at a peak. As the radial r continuously increases, the total potential gradually decreases and passes $rV(r) = 0$ again and becomes negative outside the Watson sphere. This implies that the electron-electron interaction potential, which is the only positive contribution to the potential in the total potential expression, is larger than the negative potential, which includes the contribution from the nuclues-electron and Watson sphere charge-electron interaction and the exchange-correlation effect.

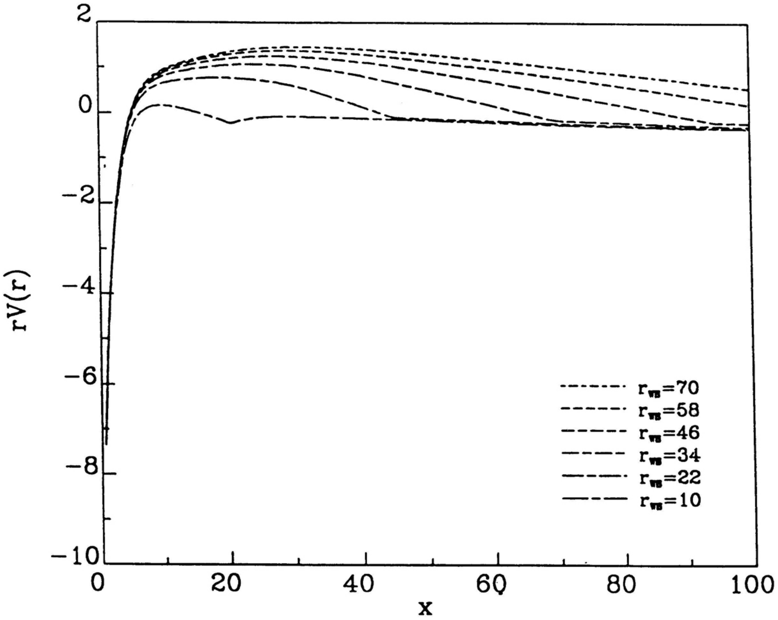

Figure 1. The potential of the outermost orbital, $2p\downarrow$, of the doubly charged negative ion of carbon, C^{2-}, vs the modified radial x

Figure 2 plots the dependence of the electron density distribution for the electron in the outermost orbital, $2p\downarrow$, of the doubly charged negative ion of carbon, C^{2-}, on the Watson sphere radius. It is clear that the electron density is gradually shifted toward a large radius, when the Watson sphere radius is increased. To keep the nor-

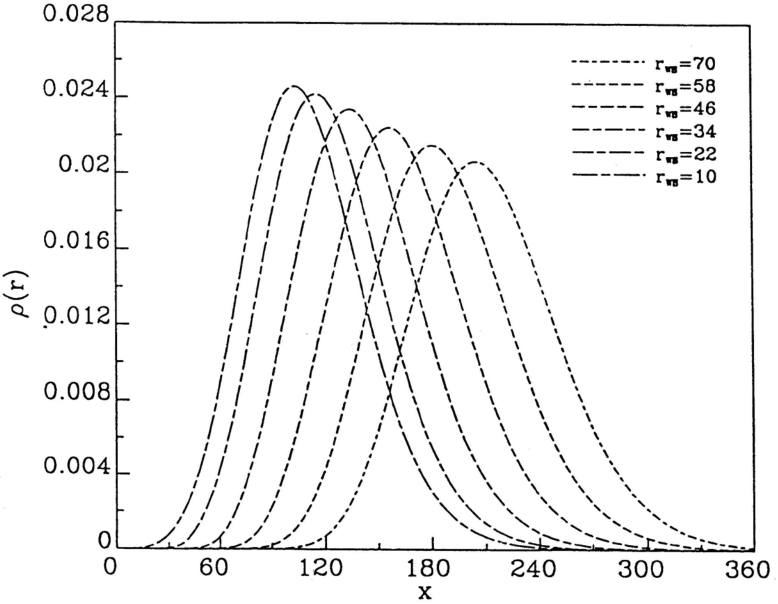

Figure 2. The dependence of the electron density distribution for the electron in the outermost orbital, $2p\downarrow$, of the doubly charged negative ion of carbon, C^{2-}, on the radius of the Watson sphere

malization of the wave function, the peak of the curve is reduced and the electron density gradually spread, as the Watson sphere size increases. The electron density distribution of a core orbital, such as the 1s orbital in C^{2-}, is not affected by changing the Watson sphere radius.

Comparing Figures 1 and 2 shows that the electron density of the outermost orbital is mainly distributed outside of the Watson sphere, when the Watson sphere radius is less than 70 a_0. Hence, the barrier of the total potential is not caused by the charge density of the electron in the outermost orbital, but is created by the constant potential generated by the charge on the Watson sphere inside the Watson sphere.

Obviously, the statistical total energy and the one-electron eigenvalue of a doubly charged negative ion in the electron-correlation corrected SIC-GX-LSD theory with the GWB Fermi-hole parameters are dependent on the Watson sphere size, when it is not large enough. Table I shows the dependence of the total energy, including the statistical total energy and the VWN correlation energy, but excluding the energy contribution from the Watson sphere, the one-electron eigenvalue, and the expectation value of the Watson sphere potential for the electron in the outermost orbital of the doubly charged negative ion of carbon, C^{2-}, on the Watson sphere radius. When the Watson sphere radius increases, the electron density spreads toward the large radial. Therefore, the electron-electron repulsive energy decreases and the nucleus-electron attractive energy decreases. Because the contribution of the former to the statistical total energy is positive and the contribution of the latter is negative, they partly cancel. The total energy excluding the Watson sphere energy (Table I) depends slightly on the Watson sphere radius and increases in size as the Watson sphere radius increases. Fur-

TABLE I

The dependence of the total energy and the one-electron eigenvalue and the expectation value of the Watson sphere potential for the outermost orbital of the doubly charged negative ion of carbon, C^{2-}*(Ry) by the SIC-GX-LSD-VWN-GWB*

rws	E_{tot}	$\varepsilon_{2p\downarrow}$	$<2p\downarrow\ \lvert Vws \rvert 2p\downarrow>$
10	-76.1276	-0.004366	-0.04009
14	-76.1292	-0.004320	-0.03838
18	-76.1309	-0.004265	-0.03654
22	-76.1327	-0.004197	-0.03462
26	-76.1346	-0.004119	-0.03274
30	-76.1364	-0.004033	-0.03094
34	-76.1381	-0.003943	-0.02927
38	-76.1398	-0.003853	
42	-76.1413	-0.003763	-0.02772
46	-76.1426	-0.003675	-0.02629
50	-76.1439	-0.003590	-0.02500
54	-76.1450	-0.003508	-0.02380
58	-76.1460	-0.003429	-0.02271
62	-76.1470	-0.003353	-0.02170
66	-76.1479	-0.003280	-0.02079
70	-76.1487	-0.003211	-0.01994

thermore, the dependence of the total energy on the Watson sphere radius decreases as the Watson sphere radius increases. For example for C^{2-} the difference of the total energies calculated with $r_{WS} = 14\ a_0$ and $r_{WS} = 18\ a_0$ is 09.0017 Ry, whereas the difference of the total energies calculated with $r_{WS} = 54\ a_0$ and $r_{WS} = 58\ a_0$ is 0.0010 Ry. However the one-electron eigenvalue for the outermost orbital of the doubly charged negative ion is strongly dependent on the Watson sphere radius and decreases in magnitude as the Watson sphere radius increases. The dependence of the expectation value of the Watson sphere potential for the electron in the outermost orbital of C^{2-} is shown in column 4 of Table I. The value decreases as the Watson sphere radius increases, because the Watson sphere potential is gradually reduced by increasing the Watson sphere radius. The real one-electron eigenvalue can be obtained by subtracting the expectation value of the Watson sphere potential, column 4 of Table I, from the calculated one-electron eigenvalue of the corresponding orbital, column 3 of Table I. Hence the real one-electron eigenvalue excluding the contribution from the Watson sphere is positive and gradually decreases when the Watson sphere radius increases.

Since the total energy, excluding the Watson sphere energy, for a doubly charged negative ion increases as the Watson sphere radius increases, the difference between the total energies of the doubly and singly charged negative ions should decrease in size, because no Watson sphere is used in calculating the singly charged ion. Table II lists the dependence of the second electron affinities for an Al on the Watson sphere radius in the electron-correlation corrected SIC-GX-LSD theory with the GWB Fermi-hole parameters. The difference of the electron affinities becomes smaller and smaller, when the Watson sphere radius becomes bigger and bigger. For instance, the difference of the electron affinity for B is -0.2437 Ry, when the Watson sphere size is increased from $2a_0$ to 4 a_0, -0.0020 Ry when the size is increased from 30 a_0 to 32 a_0 and -0.0006 Ry when the size is increased from 60 a_0 to 62 a_0. The electron affinity in the electron-correlation corrected SIC-GX-LSD theory is not significantly changed by increasing the Watson sphere radius when the Watson sphere radius is large enough and approaches a constant value. Unfortunately, no converged values were obtained for B, when the Watson sphere radius was bigger than 62 a_0. This raises the question of what is the asymptotic value of the electron affinity for B when the Watson sphere radius goes to infinity? Is it possible to fit the calculated value and then estimate its asymptotic electron affinity using any function? The behaviour of the calculated electron affinity for B is inversely proportional to the Watson sphere radius.

The simplest function worthwhile testing is

$$A = A_0 - \frac{a}{r_{\mathrm{WS}}} \tag{2}$$

where A_0 and a are constants to be determined. If the equation can fit the electron affinities calculated in the electron-correlation corrected SIC-GX-LSD theory with a large size of Watson sphere, the asymptotic value should correspond to the real electron affinity, when r_{WS} approaches infinity, that is A_0.

This approach was tested for B first. It was found that when $A_0 = -0.147$ Ry and $a = 1$ Ry/a_0, the electron affinities calculated using the Watson spheres whose radii are bigger than 30 a_0 were perfectly fitted by equation (2). The calculated and fitted results are listed in the columns 2 and 3 of Table II, respectively. The dependence of calculated electron affinities for Al on the Watson sphere is of the same behaviour as those for B. The calculated electron affinities by using different radii of the Watson spheres also can be fitted by equation (2) with $A_0 = -0.1344$ Ry and $a = 1$ Ry/a_0. The calculated and fitted electron affinities are summarized in the columns 4 and 5 of Table II, respectively.

For a test, the singly negative ions X^- were calculated with a Watson sphere radius r_{WS} and $q = +1$: when the asymptotic result was applied the EA(1) were identical with the values calculated without the Watson sphere. Then the doubly charged negative ions $X^=$ were calculated with r_{WS} and $q = +2$ and gave the same asymptotic results as the calculation with r_{WS} and $q = +1$ which are reported. The same behaviour can be applied to other doubly charged negative ions of the second and third period elements. The calculated electron affinities can be fitted well by equation (2) with $A_0 = -0.0047$ Ry and $a = 0.9$ Ry/a_0 for C, $A_0 = -0.0083$ Ry and $a = 0.7$ Ry/a_0 for Si, $A_0 = -0.0237$ Ry and $a = 1.425$ Ry/a_0 for N, $A_0 = -0.0458$ Ry and $a = 1.395$ Ry/a_0 for P, $A_0 = -0.3606$ Ry and $a = 0.6353$ Ry/a_0 for O, and $A_0 = -0.2012$ Ry and $a = 0.56$ Ry/a_0 for S. The electron affinities are presented in Table III and compared with the HF calculation given by Clementi and McLean[19] and the CI calculations with the single and double substitutions obtained by Kalcher[22]. The calculated results are very different and those of HF and CI(SD) suspiciously constant between very different ions with very different EA(1). The present results are the only ones which are part of a large body of established results and should be correct. There are no experimental values for free atoms available for comparison, but all these calculations show that the doubly charged negative ions of the second and third period elements are unstable in gas phase, and give insight into the energy required to generate the doubly charge ions. The variation in the EA(2) with occupancy in the SIC-GX-LSD-VWN (GWB) theory reflected the VWN correlation effect when the electrons doubly occupy an orbital; when the electrons occupy different orbitals the exchange effect predominates.

TABLE II

The dependence of the second electron affinities (Ry) of B and Al on the Watson sphere radius (a_o)*, and fitting by a function of* $A = A_o - a/rws$ *with* $A = -0.1147$ *Ry and* $a = 1$ *Ry* a_o^{-1} *for B and* -0.1344 *Ry and* $a = 1$ *Ry* a_o^{-1} *for Al*

rws	B SIC-GX-LSD-VWN-GWB	Fitting	Al SIC-GX-LSD-VWN-GWB	Fitting
2	–0.5835	–0.6147	–0.5839	–0.6344
4	–0.3398	–0.3647	–0.3577	–0.3844
6	–0.2613	–0.2814	–0.2771	–0.3011
8	–0.2248	–0.2397	–0.2397	–0.2594
10	–0.2040	–0.2147	–0.2193	–0.2344
12	–0.1903	–0.1980	–0.2063	–0.2177
14	–0.1805	–0.1861	–0.1971	–0.2058
16	–0.1730	–0.1772	–0.1902	–0.1969
18	–0.1671	–0.1703	–0.1846	–0.1900
20	–0.1623	–0.1647	–0.1802	–0.1844
22	–0.1583	–0.1602	–0.1745	–0.1799
24	–0.1547	–0.1564	–0.1733	–0.1761
26	–0.1501	–0.1532	–0.1706	–0.1729
28	–0.1489	–0.1504	–0.1676	–0.1701
30	–0.1474	–0.1480	–0.1666	–0.1677
32	–0.1454	–0.1459	–0.1647	–0.1656
34	–0.1437	–0.1441	–0.1630	–0.1638
36	–0.1421	–0.1425	–0.1615	–0.1622
38	–0.1407	–0.1410	–0.1600	–0.1607
40	–0.1394	–0.1397	–0.1587	–0.1594
42	–0.1384	–0.1385	–0.1577	–0.1582
44	–0.1373	–0.1374	–0.1566	–0.1571
46	–0.1364	–0.1364	–0.1557	–0.1561
48	–0.1354	–0.1355	–0.1546	–0.1552
50	–0.1347	–0.1347	–0.1543	–0.1544
52	–0.1339	–0.1339	–0.1535	–0.1536
54	–0.1332	–0.1332	–0.1528	–0.1529
56	–0.1325	–0.1326	–0.1521	–0.1523
58	–0.1319	–0.1319	–0.1516	–0.1516
60	–0.1314	–0.1314	–0.1510	–0.1511
62	–0.1308	–0.1308	–0.1505	–0.1505

Consequently from B to C and Al to Si, the exchange energy stabilizes the doubly negative ion while from C to O and Si to S the correlation energy decreases the stability of the doubly negative ion. This trend parallels than in the M^-, M^O, M^+, M^{2+}, and M^{3+} ions[30,46,47].

CONCLUSION

It can be seen that with the aid of a Watson sphere, the SCF procedure can be carried out, when the Watson sphere radius is not too big. The dependence of the second electron affinities in the electron correlation corrected SIC-GX-LSD theory with the GWB Fermi-hole parameters on the Watson sphere radius is as in equation (2), and can be approximated by the asymptotic values of equation (2) as the Watson sphere radius goes to infinity.

TABLE III

The second electron affinities EA (2) (Ry) of B, C, N, O, Al, Si, P and S obtained by fitting the calculated value in the electron correlation corrected SIC-GX-LSD theory with the GWB Fermi-hole parameters, compared with other theoretical calculations

Atom	SIC-GX-LSD[a]	HFb	CI(SD)c
B	−0.1147		
C	−0.0047		
N	−0.0237	−0.4540	
O	−0.3606	−0.4440	
Al	−0.1344		−0.0542
Si	−0.0083		−0.0612
P	−0.0458		−0.0612
S	−0.2012		−0.0499

[a] The present work SIC-GX-LSD-VWN-(GWB) theory

[b] Reference 19;

[c] Reference 22.

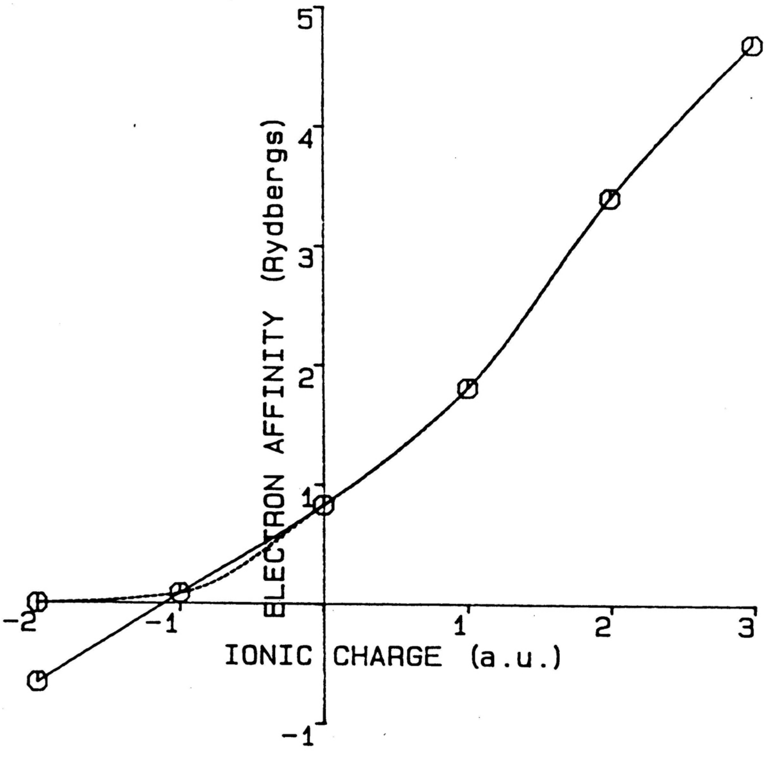

Figure 3.

Qualitatively, the signs of the second electron affinities in the electron correlation corrected SIC-GX-LSD theory with the GWB parameters are the same as those obtained by the HF and CI(SD) calculations. The doubly charged negative ions in their ground states are unstable in the gas phase for the second and third period elements which involve one orbital in going from the neutral atom to its doubly charged negative ion. They are similar to the values calculated for small molecules in sign and magnitude[37-39] and the method should prove useful for solid state and molecular calculations.

In Figure 3 the results for carbon electron affinities for C^{3+}, C^{2+}, C^{+}, C^{0}, C^{-}, and C^{2-} are plotted. The C^{2-} are from the present paper and the other ions from references 30 and 46. The second value of C^{2-} was calculated using the Watson sphere which gave the experimentally measured values of M^2 in the ionic crystal and equaled the experimentally measured interatomic distance in the ionic crystal. Consequently in moving r_W from the experimental value in an ionic crystal to ∞ for the corresponding doubly charged negative atom, the EA(2) of the doubly negative ions follow the same pattern as in ionic crystals[46]Pt but are considerably smaller. The figure shows the EA(2) smoothly related to both $EA(2)_{rW=\infty}$ and $EA(2)_{rW=\text{interatomic}}$.

The electronic structure of a doubly-charged negative ion is complicated, perhaps including the coupling of the valence and continuum states and forming the metastable doubly-charged negative ion states. But no matter what state the system would be in, it should obey the Schrödinger equation. The present method is a simple technique to predict second electron affinities of atoms, and allow calculation of electronegativities and hardness of atoms[30] and groups[33].

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SAŽETAK

Stabilnost dvostruko nabijenih negativnih iona u okviru teorije funkcionala gustoće

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Izračunani su drugi elektronski afiniteti negativno nabijenih iona atoma B, C, N, O, Al, Si, P i S primjenom poopćene teorije funkcionala lokalne spinske gustoće. Pri tome je korišten model pozitivno nabijene kugle (Watson), čiji je radijus postupno povećavan do neizmjernosti. Rezultati pokazuju da su dvostruko nabijeni negativni ioni nestabilni, ali manje nego u ionskim kristalima.