

## Infinite screening and cluster calculations of ionization potentials

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Using beryllium as a model system it is suggested that cluster simulations of core-electron ionization potentials in metals should be carried out with the same number of electrons in the initial and final states.

### INTRODUCTION

Along with the rapid development of quantum-chemical methods there has been a growing interest in cluster simulations of metal properties as well as cluster properties that converge towards those of the solid as the size of the cluster increases. The main difference between these two approaches is that, when carrying out calculations, the geometry of the solid is used for the clusters in the simulation case. This is the approach we have chosen in the present work. Hereby symmetry-related properties, like orbital structure, selection rules, etc., will be more closely related to the solid than if the structure of the equilibrium conformation is adopted. Since band-structure calculations presuppose a periodic lattice they are not directly fit for analyzing, e.g., properties of point defects or local impurities. This opens a broad niche for cluster calculations, containing many interesting topics, for example, crystallization of materials, chemisorption, and other studies relating to the formation and breaking of chemical bonds.<sup>1-3</sup> The chemical stability and geometry of clusters<sup>4-6</sup> is a popular topic for quantum-chemical calculations as well as electronic structure and ionization potentials,<sup>7,8</sup> etc. There is also an increasing number of experimental investigations of the properties of metal-atom clusters.<sup>9,10</sup> The papers referred to are only a few examples of the work performed in these fields of research.

In the present work we address how the core-electron ionization energies can be simulated by cluster calculations. Such calculations are performed in order to account for the extraatomic screening of the core ionized atom. Nicolaides *et al.*<sup>11</sup> have simulated the Be 1s ionization potential (IP) in beryllium bulk metal, using a Be<sub>13</sub> cluster. The IP of the cluster is claimed to be a good approximation to the one of the metal. Recently the same method has been applied for Mg and Ca by Zdetsis.<sup>12</sup> In the present work we suggest that cluster simulations of metallic core ionization potentials should be carried out with an equal number of electrons in the initial and final states of the photoionization. In this way the complete screening of the core-hole state is simulated in the cluster calculation by assuming a neutral, core excited final state. We have chosen beryllium and a self-

consistent-( $\Delta$ SCF) level of approximation to demonstrate the validity of the model. The model we present should apply for all metal clusters.

We also investigate the validity of the  $Z + 1$  approximation<sup>13</sup> for Be, which is not evident due to the facts that the 1s orbital is comparatively shallow and that, considering the core excited case, the single electron in the 2p orbital is easily polarizable and sensitive to the change in the core. We investigate in this paper the cluster Be<sub>1</sub>-Be<sub>6</sub>, Be<sub>10</sub>, and Be<sub>13</sub>. One motivation for this investigation is also that the experimental surface core-level shift<sup>14</sup> is of opposite sign relative to the theoretically predicted shifts.

### COMPUTATIONAL

Beryllium 1s ionization and excitation potentials for cluster sizes 1-6, 10, and 13 are presented in this paper. The clusters have the same geometry as solid beryllium. All calculations were performed on a  $\Delta$ SCF level using a Dunning-Hay double- $\zeta$  (6111/41) basis set, consisting of four *s*-type and two *p*-type contracted Gaussians, on the Be atom chosen as the site of the core hole and a Pople single- $\zeta$  (631/3) basis set, consisting of three *s*-type and one *p*-type contracted Gaussians, on the remaining atoms in the cluster. The basis sets are displayed in Tables I and II.

Calculations were performed with a fully second-order optimization algorithm.<sup>15</sup> Using this algorithm a relaxed core-hole state was produced by first performing a calculation where the singly occupied core orbital is kept frozen, making the core-hole state correspond to the first root in the limited variational space. This is a necessary measure in order to avoid variational collapse, since with free variation the core-hole state corresponds to an infinite root, or, in a basis set, a root with an unknown order number. The resulting wave function is in the local energy region of the full variational space and a second calculation relaxing the core orbital will take the energy to the final minimum by a Newton-Raphson procedure which does not require knowledge *a priori* of the root index.<sup>16</sup> For the systems calculated in this work the contribution to the total energy from the core-hole orbital relaxation is of the order of 0.03 a.u.

TABLE I. Double- and single- $\zeta$  basis sets used in the calculation.

Orbital	Exponent	Coefficient
Dunning-Hay double- $\zeta$ (6111/41) basis set		
1s	1741.000	0.001 305
	262.1000	0.009 955
	60.330 00	0.048 031
	17.620 00	0.158 577
	5.933 000	0.351 325
	0.859 000	0.160 490
1s	2.185 000	1.000 000
2s	0.180 600	1.000 000
2s	0.058 350	1.000 000
2p	6.710 000	0.016 378
	1.442 000	0.091 553
	0.410 300	0.341 469
	0.139 700	0.685 428
2p	0.049 220	1.000 000
Pople single- $\zeta$ (631/3) 6-31G		
1s	1267.070	0.001 940
	190.3560	0.014 786
	43.295 90	0.071 795
	12.144 20	0.236 348
	3.809 230	0.471 763
	1.268 470	0.355 183
2s	5.693 880	-0.028 876
	1.555 630	-0.177 565
	0.171 855	1.071 630
2s	0.057 181	1.000 000
2p	5.693 880	0.004 835
	1.555 630	0.144 045
	0.171 855	0.949 692

For atomic Be, additional calculations were performed at the full configuration-interaction (CI) level for the ground state. The core ionized and core excited states were calculated with the full CI space reduced by a single-occupancy requirement for the core-hole orbital, which, however, was optimized by including rotations with the active orbitals. The single-occupancy restriction for the core orbital is necessary in order to solve the secular equation for large CI spaces. This has been found to be well motivated from perturbation-theory analysis of core-electron ionization potentials.<sup>17</sup>

The clusters 1–6 and 10 were calculated without considering symmetry, thereby obtaining their correct ground-state electron configurations directly from the variationally optimal wave functions. For the core-hole states of Be<sub>13</sub> the calculations were reduced in size by applying C<sub>2v</sub> symmetry to the problem. In order to determine the ground-state configuration for Be<sub>13</sub> the ground-state energy was first calculated without applying symmetry. The calculation was thereafter repeated for some C<sub>2v</sub> configurations until the value was reproduced. Geometries and basis sets are presented in Tables I and II.

The electronic structure of the beryllium atom contains a 2s-2p resonance, which is important to account for in

calculations of finer properties like polarizabilities and cohesive energies. The latter effects have been simulated in large-scale correlated calculations on two-, three-, and four-membered beryllium clusters by Harrison and Handy.<sup>4</sup> However, the computational effort in all-electron methods grows rapidly to prohibitive levels for larger clusters, and will also be afflicted by size consistency

TABLE II. Geometries of the calculated Beryllium clusters. The bond lengths are 4.319 and 4.205 a.u., as in the metal. Atom no. 1 in each cluster is core ionized and is described by a Dunning and Hay double- $\zeta$  basis set in order to better relax the core hole. All other atomic sites are equipped with a Pople 6-31G single- $\zeta$  basis set.

Cluster	Atom	Coordinates in atomic units		
		X	Y	Z
Be <sub>2</sub>	1	0.000 000	0.000 000	0.000 000
	2	4.319 000	0.000 000	0.000 000
Be <sub>3</sub> <sup>a</sup>	1	0.000 000	0.000 000	0.000 000
	2	3.740 360	-2.159 500	0.000 000
	3	3.740 360	2.159 500	0.000 000
Be <sub>4</sub> <sup>b</sup>	1	0.000 000	0.000 000	0.000 000
	2	0.000 000	2.493 576	3.385 500
	3	2.159 500	-1.246 788	3.385 500
	4	-2.159 500	-1.246 788	3.385 500
Be <sub>5</sub>	1	0.000 000	0.000 000	3.385 500
	2	0.000 000	2.493 576	0.000 000
	3	2.159 500	-1.246 788	0.000 000
	4	-2.159 500	-1.246 788	0.000 000
	5	0.000 000	0.000 000	-3.385 500
Be <sub>6</sub>	1	0.000 000	0.000 000	3.385 500
	2	0.000 000	2.493 576	0.000 000
	3	2.159 500	-1.246 788	0.000 000
	4	-2.159 500	-1.246 788	0.000 000
	5	0.000 000	0.000 000	-3.385 500
	6	0.000 000	-4.319 000	3.385 500
Be <sub>10</sub> <sup>b</sup>	1	0.000 000	2.493 576	0.000 000
	2	0.000 000	0.000 000	3.385 500
	3	2.159 500	-1.246 788	0.000 000
	4	-2.159 500	-1.246 788	0.000 000
	5	0.000 000	-2.493 576	-3.385 500
	6	2.159 500	1.246 788	-3.385 500
	7	-2.159 500	1.246 788	-3.385 500
	8	4.319 000	-2.493 576	-3.385 500
	9	-4.319 000	-2.493 576	-3.385 500
	10	0.000 000	4.987 152	-3.385 500
Be <sub>13</sub> <sup>c</sup>	1	0.000 000	0.000 000	0.000 000
	2	0.000 000	4.319 000	0.000 000
	3	3.740 364	2.159 500	0.000 000
	4	-3.740 364	2.159 500	0.000 000
	5	0.000 000	-4.319 000	0.000 000
	6	-3.740 364	-2.159 500	0.000 000
	7	3.740 364	-2.159 500	0.000 000
	8	2.493 576	0.000 000	3.385 500
	9	-1.246 788	2.159 500	3.385 500
	10	-1.246 788	-2.159 500	3.385 500
	11	-2.493 576	0.000 000	-3.385 500
	12	1.246 788	2.159 500	-3.385 500
	13	1.246 788	2.159 500	-3.385 500

<sup>a</sup>Triangular structure.

<sup>b</sup>Tetrahedral structure.

<sup>c</sup>hcp structure.

problems for the variational-type calculations when full CI is beyond the computational capacity. The  $\Delta$ SCF level of approximation employed in the present work is known to give very reasonable ionization potentials for light atoms, since the electronic correlation in the valence shell is mainly preserved.

When checking the  $Z + 1$  approximation for beryllium the equivalent core state, i.e., the lowest ionic state of boron, was obtained by adding a positive charge to the site of the double- $\zeta$  basis set and including one extra electron in the cluster. Basis sets and geometries were identical to those used in the corresponding beryllium-cluster calculations. The atomic boron states were also calculated at the FCI level.

### CORE IONIZATION OF METAL CLUSTERS AND SOLIDS

XPS experiments on solid metals relate the binding energy to the Fermi level and therefore the work function is often added to obtain a value comparable to calculated 1s ionization energies for clusters. One crucial difference between the metal and the cluster in their ionized states is the effect of the residual positive charge. In large core-ionized clusters the positive charge will be distributed mainly over the surface. The potential inside a sphere due to a surface charge is inversely proportional to the radius. The electrostatic energy contribution from the positive charge is thus proportional to  $M^{-1/3}$ , where  $M$  is the number of atoms in the close-packed cluster.

The final states of the metal produced by core ionization and core excitation are identical,<sup>18</sup> and experimental results from Fermi-level-related XPS and x-ray absorption<sup>19</sup> will be the same. Our aim with this work is to demonstrate that this fact should be accounted for *a priori* in a cluster simulation of metallic ionization potentials, i.e., that a core-excited cluster describes the core-ionized metal better than the core-ionized cluster does.

Figure 1 displays a schematic picture of the ionization processes discussed. In the metal case the core hole is perfectly screened by electrons at the Fermi level [Fig. 1(b)]. In the core-“excited” state [Fig. 1(a)] of a cluster an electron is brought in from the vacuum level in order to achieve perfect screening. This state is, apart from the photoelectron, identical to a core-excited state. The total energies of the core-excited  $N$ -electron and core-ionized  $(N - 1)$ -electron states are

$${}^s E^*(N) = E(N) - \epsilon_{\text{core}}(N) + \epsilon_{\text{LUMO}}(N) + {}^s V_c(\text{core, LUMO}, N) + {}^s E_{\text{rel}}^*(N), \quad (1a)$$

$$E^*(N - 1) = E(N) - \epsilon_{\text{core}}(N) + E_{\text{rel}}^*(N - 1). \quad (1b)$$

The ionization energies corresponding to both cases are defined as

$${}^s I^{\text{exc}} \equiv {}^s E^*(N - 1) - E(N), \quad (2a)$$

$$I^{\text{ion}} \equiv E^*(N) - E(N). \quad (2b)$$

$E$  denotes total energies,  $E_{\text{rel}}$  relaxation energies, and  $\epsilon$  denotes orbital energies. LUMO and HOMO are abbreviations for the lowest unoccupied molecular orbital and

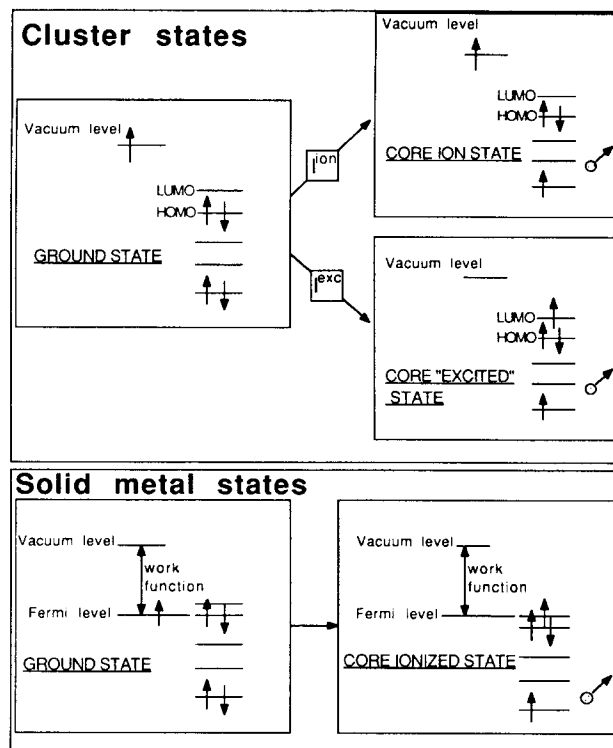


FIG. 1. (a) Top: core ionization of clusters. In the case of the core “excited” state, an extra electron is brought in from the vacuum level in order to achieve optimum screening of the core hole. (b) Bottom: Core ionization in solid metal. The core hole is perfectly screened by electrons at the Fermi level.

the highest occupied molecular orbital. Core-hole-related entities are marked by an asterisk and spin dependency is represented by an  $s$  in the left-hand upper index. The extra electron in the core-excited case [Eq. 1(a)] can couple in different ways to the open core adding the spin interaction energy of the frozen-state core ion,  ${}^s V_c(\text{core, LUMO}, N)$ . Also the relaxation energy will be spin dependent. The difference in energy between these states is

$$\Delta \equiv {}^s E^*(N) - E^*(N - 1) = \epsilon_{\text{LUMO}}(N) + {}^s V_c(\text{core, LUMO}, N) + {}^s E_{\text{rel}}^*(N) - E_{\text{rel}}^*(N - 1). \quad (3a)$$

$$+ {}^s E_{\text{rel}}^*(N) - E_{\text{rel}}^*(N - 1). \quad (3b)$$

For the solid metal with a work function  $\Phi$

$$N \rightarrow \infty \implies \epsilon_{\text{LUMO}}(N) \rightarrow \Phi \quad (4a)$$

$$\implies {}^s V_c(\text{core, LUMO}, N) \rightarrow 0 \quad (4b)$$

$$\implies {}^s E_{\text{rel}}^*(N) \rightarrow E_{\text{rel}}^*(N) \rightarrow E_{\text{rel}}^*(N - 1), \quad (4c)$$

hence

$$N \rightarrow \infty \implies \Delta \rightarrow \Delta = \Phi. \quad (5)$$

Therefore the ionization energy  ${}^s I^{\text{exc}}$  should be compared to the Fermi-level-related core-ionization energy of the metal. The statement in (4b), that the spin splitting van-

ishes as the system grows very large, is supported by the fact that in the Hartree-Fock approximation the energies of the triplet and singlet states are

$${}^1E = E_k - D, \quad (6a)$$

$${}^3E = E_k + D, \quad (6b)$$

and that  $D$ , the exchange integral, is positive and has the property<sup>20</sup>

$$D = O(a^2/\Omega), \quad (7)$$

where  $a$  is a typical lattice constant and  $\Omega$  is the volume of the whole crystal. Disregarding cluster effects, which will be dominating for small clusters, the spin splitting should thus be inversely proportional to the number of atoms in the cluster.

For the Be atom we have performed  $\Delta$ SCF calculations as well as full CI calculations (see computational section). The results are discussed together with those of the B atom below. There we also discuss correlation effects and the quality of the Dunning-Hay double- $\zeta$  basis set.

Figure 2 presents some calculated results from Table III graphically for  $\text{Be}_1$ – $\text{Be}_6$ ,  $\text{Be}_{10}$ , and  $\text{Be}_{13}$ . The work function of beryllium metal, 3.9 eV, has been subtracted from the calculated  $I^{\text{ion}}$ . Hereby  ${}^3I^{\text{exc}}$  and  $I^{\text{ion}}$  are converging towards the same value in the graph. In the figure an experimental value for bulk core ionization,<sup>1</sup> 111.7 eV,<sup>14</sup> is presented to provide a reference level. It is clearly seen in Fig. 1 that  $I^{\text{exc}}$  for a cluster is a better approximation to the metal core-ionization energy than  $I^{\text{ion}}$  for the same cluster, as we expected. This applies for all clusters investigated. The curves do not converge smoothly towards the ionization energy for the solid due to cluster effects. For example,  $\text{Be}_4$  has greater excitation and ionization energies than  $\text{Be}_5$ . However, the perturbations are too small to affect the main trend of convergence. For all clusters the core hole has been placed on an atom with as large a coordination number as possible.

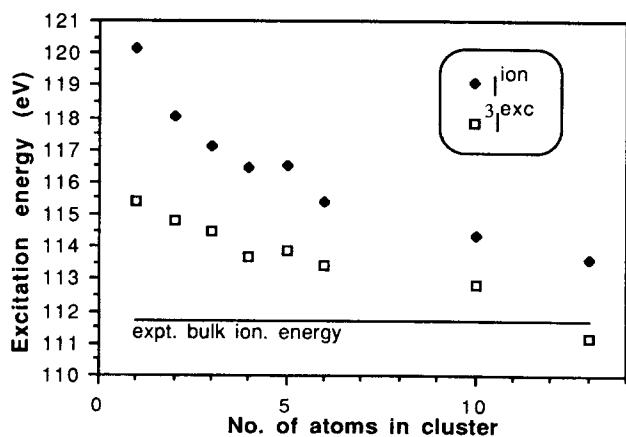


FIG. 2. Predicted core ionization ( $I^{\text{ion}}$ ) and core excitation (to triplet state) ( ${}^3I^{\text{exc}}$ ) energies for Be clusters. The experimentally determined work function for Be metal, 3.9 eV, has been subtracted from the core-ionization values so that both graphs converge towards the same value in the plot.

For  $\text{Be}_{13}$  we have also calculated the ionization potential from an atom with the smallest coordination number. As can be seen in Table III, the ionization and excitation energies will in this case be close to those of  $\text{Be}_6$ . This indicates that the number of nearest neighbors is important, and since the maximum number is reached for  $\text{Be}_{13}$  (central atom) we expect that the rate of convergence in the graph towards bulk ionization energy will diminish after this point. This argument is supported by the fact that  ${}^3I^{\text{exc}}$  is in the same region as the experimental values for  $\text{Be}_{13}$ . Furthermore, the experimental shift between the Be 1s ionization energies for the atom (vacuum-level related) and the metal (Fermi-level related) is 11.9 eV. The difference in the calculated core-ionization energy for  $\text{Be}_1$  and core-excitation energy for  $\text{Be}_{13}$  is  $[I^{\text{ion}}(\text{Be}_1) - {}^3I^{\text{exc}}(\text{Be}_{13})] = 12.8$  eV. Hence we conclude that the difference in core ionization and excitation energy for  $\text{Be}_{13}$  has two main contributions: the work function of the metal and the screening achieved by the extra electron in the core-excited cluster.

Nicolaides *et al.*<sup>11</sup> predict a vacuum-level ionization energy of 115.5 eV for  $\text{Be}_{13}$  (including relativistic and correlation contributions, set to 0.5 eV), which is not far from the experimental value of 115.6 eV (Ref. 21) for solid Be metal. Unfortunately, they do not present any calculated total energies, which makes it difficult to appreciate the quality of their results. In fact, simulating perfect screening for  $\text{Be}_{13}$  by adding an extra electron to the final-state cluster shifts the ionization energy by  $I^{\text{ion}} - {}^3I^{\text{exc}} - \Phi = 2.4$  eV according to our calculation. ( $\Phi$  is the work function for Be.) To a first order this is the difference between the  $\text{Be}_{13}$  and solid Be vacuum-level-related core-ionization energies. Hence the ionization energy presented by Nicolaides *et al.* seems to be approximately 2 eV too close to the experimental metal bulk ionization energy, since it is not compensated for perfect screening.

Using sufficiently large clusters it is also possible to study the difference between bulk and surface core-ionization energies. The  $\text{Be}_{13}$  cluster has one “bulk” atom whereas the other 12 atoms are located at the surface of the cluster. These “surface” atoms have a rather small coordination number so in this sense they represent the properties for a non-close-packed Be surface. As seen from Table III a positive surface shift of around 2 eV is calculated for the cluster, in rather large disagreement with the experimental value. This may be due either to correlation effects having been omitted in the calculation, or the cluster being still too small to simulate the metal properties in this case.

Surface core-level shifts have been observed for a large number of metals. Shifts to both higher and lower energies have been observed. These shifts can be interpreted in terms of cohesive properties of the initial and the core-ionized final-state atoms. Using a  $Z + 1$  approach all observed metallic surface core-level shifts have been well reproduced.<sup>22</sup> The only exception so far is the beryllium metal for which a shift of 0.5 eV to lower binding energy is observed for the surface, whereas the theory predicts a shift to higher energies. Using the present cluster approach, we will therefore investigate if this

TABLE III.  $\Delta$ SCF ground-state total energies and core-excitation and -ionization energies for Be clusters. The core-excitation energies predicted by the  $Z + 1$  approximation are also presented. Geometries and basis sets are displayed in Tables I and II. The core-ionization energies subtracted by the lowest valence-ionization potential for the corresponding ( $Z + 1$ )-substituted cluster. The latter values are from Table V.

No. of atoms in cluster	Ground-state total energy (a.u.)	Calculated $\Delta$ SCF energies			
		Core-ioniza- tion energy (eV)	singlet (eV)	Excitation energies triplet (eV)	$Z + 1$ approx. (eV)
2	-23.120 366	121.962	114.946	114.836	115.261
3	-43.695 796	121.0 <sup>a</sup>	115.003	114.489	114.7
4	-58.309 775	120.337	114.492	113.719	114.210
5	-72.864 556	120.432	114.497	113.853	114.607
6	-87.411 515	119.277	113.569	113.452	113.360
10	-145.821 742	118.244	112.914	112.843	113.085
13 (bulk <sup>b</sup> )	-189.705 804	117.513	111.468	111.208	111.521
13 (surf. <sup>c</sup> )	-189.708 341	118.885	113.521	113.312	113.528

<sup>a</sup>Estimated value, due to variational collapse of relaxed core-hole orbital state. Since the contribution to the total energy from the core-hole orbital relaxation is approximately 0.03 a.u. for all the other clusters it is set to the same value for Be<sub>3</sub>.

<sup>b</sup>Double- $\zeta$  basis set and core hole located on the center ("bulk") atom.

<sup>c</sup>Double- $\zeta$  basis set and core hole located on a surface site. (Position 8 of Be<sub>13</sub>. See Table II.)

discrepancy could be explained by a shortcoming of the  $Z + 1$  approximation for Be.

#### THE $Z + 1$ APPROXIMATION

In the atomic case, if the  $Z + 1$  approximation applies and spin coupling is ignored, the energy difference between the core-excited and core-ionized state of Be should equal the first ionization energy of boron. Since the excited electron in Be will spin couple with the remaining core electron this will split the energy of the excited species, supplying boundaries to the boron

valence-ionization energy if the approximation applies. Equally, subtracting the boron valence-ionization energy from the Be core-ionization energy should leave a result which is between  $^3I^{\text{exc}}$  and  $^1I^{\text{exc}}$ .

The calculated energies for the Be and B atoms are displayed in Table IV. For Be, the  $\Delta$ SCF calculations produce total energies approximately 3 eV above the experimental total energies for the investigated states. A comparison with the full CI values indicates that the errors from ignoring electron correlation and the inadequacy of the double- $\zeta$  basis set are equal in magnitude. Calculated excitation and ionization energies for Be are

TABLE IV. Calculated and experimental energies for the Be and B atoms. The FCI column contains results from full CI calculations (see computational section). In the last column, the total energies are produced by summing up atomic ionization potentials.

Entity	Final state	Total (a.u.) and excitation energies (eV)		
		$\Delta$ SCF	FCI	Expt. <sup>a</sup>
$E_{\text{tot}}$	Be $1s^2 2s^2 \ ^1S$	-14.570 907	-14.628 587	-14.668
$E_{\text{tot}}$	Be <sup>+</sup> $1s 2s^2 \ ^2S$	-10.012 633	-10.073 677	-10.127 <sup>b</sup>
$E_{\text{tot}}$	Be $1s 2s^2 2p \ ^3P$	-10.330 909	-10.376 521	-10.466 <sup>b</sup>
$E_{\text{tot}}$	Be $1s 2s^2 2p \ ^1P$	-10.305 401	-10.350 840	-10.426 <sup>b</sup>
$I^{\text{ion}}$	Be <sup>+</sup> $1s 2s^2 \ ^2S$	124.038	123.947	123.56
$^3I^{\text{exc}}$	Be $1s 2s^2 2p \ ^3P$	115.377	115.706	114.3
$^1I^{\text{exc}}$	Be $1s 2s^2 2p \ ^1P$	116.071	116.405	115.4
$I^{\text{exc}} (Z + 1)^c$		115.958	116.215	115.26 <sup>b</sup>
$E_{\text{tot}}$	B $1s^2 2s^2 3p \ ^2P$	-24.385 131	-24.429 656	-24.657
$E_{\text{tot}}$	B $1s^2 2s^2 \ ^2S$	-24.088 195	-24.145 494	-24.352 <sup>b</sup>
$I^{\text{ion}}$	B $1s^2 2s^2 \ ^1S$	8.080	7.732	8.296

<sup>a</sup>Excitation and ionization energies for Be from M. O. Krause and C. D. Caldwell, Phys. Rev. Lett. **59**, 2736 (1987); J. Phys. (Paris) Colloq. **48**, C9-473 (1987), and private communication. Ionization energy for B from CRC Handbook of Physics (Chemical Rubber Co., Cleveland, Ohio, 1968-1969), p. E-79.

<sup>b</sup>Derived through combination of experimental values.

<sup>c</sup>Excitation energy predicted by the  $Z + 1$  approximation.

TABLE V.  $\Delta$ SCF ground-state total energies and first valence-ionization energies for  $B + Be_{n-1}$  clusters. Be double- $\zeta$  basis set (Dunning and Hay) used for B. Geometries and basis sets are the same as for the pure beryllium clusters (Tables I and II).

No. of atoms in cluster	Calculated $\Delta$ SCF energies	
	Ground-state total energy (a.u.)	Valence-ion- ization energy (eV)
2	-38.954 960	6.701
3	-53.539 825	6.260
4	-68.164 023	6.127
5	-82.708 784	5.825
6	-97.298 507	5.917
10	-155.709 189	5.159
13 (bulk <sup>a</sup> )	-199.651 490	5.992
13 (surf. <sup>b</sup> )	-199.565 433	5.357

<sup>a</sup>Boron atom located at the center ("bulk") site. (Position 1 of  $Be_{13}$ . See Table II.)

<sup>b</sup>Boron atom located at a surface site. (Position 8 of  $Be_{13}$ . See Table II.)

0.5–1 eV too high using  $\Delta$ SCF. The results produced using the Dunning-Hay double- $\zeta$  basis set differ by less than 0.04 a.u. from earlier, more extensive, calculations on the Be atom.<sup>23–26</sup> Since the basis set used is optimized for Be, the results are of a lower quality in the case of B. Even so, the errors largely cancel when comparing different states, resulting in an acceptable value of the ionization energy.

Total ground-state energies and valence-ionization potentials for the  $Z + 1$  clusters are tabulated in Table V. According to our calculations the  $Z + 1$  approximation does apply for Be, using the definition above. In Table III we display core-excitation energies for the clusters  $Be_2$ – $Be_6$ ,  $Be_{10}$ , and  $Be_{13}$ , directly calculated as well as predicted by subtracting the first valence-ionization ener-

gies of the corresponding  $(Z + 1)$ -atom clusters from the core-ionization energies. The  $Z + 1$  approximation is reasonable for all those clusters. It may be argued, though, that the practical use of the approximation on smaller clusters is limited due to the large spin splittings. As the  $Z + 1$  approximation applies, it provides no explanation for the disagreement between the calculated and experimental surface shifts. This is therefore still an open question which calls for further theoretical as well as experimental work on Be surfaces.

## SUMMARY

Metallic screening has been studied using separate state self-consistent-field calculations on small Be clusters. The excitation energy of a core-excited cluster is found to converge faster towards the Fermi-level-related core-ionization energy of the metal than the core-ionization energy converges towards the vacuum-level-related core-ionization energy of the metal. This is due to the fact that in the metal the core hole is perfectly screened by the conduction electrons and the residual positive charge is spread out over the entire metal surface.

We have also investigated the validity of the  $Z + 1$  approximation for Be and found it without greater errors. The greatest error is the singlet-triplet spin splitting of the core-ionized Be cluster, which is not reproduced by the corresponding  $Z + 1$  cluster. This splitting is expected to diminish proportionally to the inverse of the number of atoms in the cluster.

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