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Dissociation channels of $Na_N{}^+$ clusters $(3 \leq N \leq 37)$

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The dissociation of $Na_N{}^+$ clusters $(N \leq 37)$ has been studied using two cluster models and two different approximations to the exchange and correlation effects. First we show that the jellium model with the usual local-density approximation to exchange and correlation leads to dissociations mostly involving Na_2 and Na_8. This prediction does not agree with recent experimental results, which indicate that most $Na_N{}^+$ clusters dissociate emitting a neutral monomer. The explicit introduction of the ions eliminates many dissociations involving Na_2 in favor of the channel involving a Na monomer. Furthermore, a nonlocal description of exchange and correlation lowers the stability of Na_8 in favor, again, of dissociation through the monomer channel. In summary, the combined effect of these two improvements leads to a satisfactory description of the dissociation of $Na_N{}^+$ in comparison with experiment.

I. INTRODUCTION

The dynamics of the dissociation of energetic sodium cluster ions ($Na_N{}^+$) has been recently studied by Bréchignac *et al.*[1] Hot clusters in the size range $3 \leq N \leq 37$ evaporate neutral monomers (Na) and neutral dimers (Na_2). If the internal energy of the metastable hot $Na_N{}^+$ cluster is randomly distributed among the internal modes, then a measurement of the rate of dissociation permits us to obtain the binding energy of the fragment[1,2] and the fragment with the smallest binding energy is the preferred one. In this way, by measuring dissociation rates, Bréchignac *et al.* have obtained the binding energies of an atom and a dimer in Na-cluster ions with different sizes. Theory and experiment can then be compared directly, instead of comparing theoretical stabilities with abundance spectra,[3] which was the traditional approach until now.

Binding energies are available from *ab initio* calculations of (ground-state) cationic clusters for $N \leq 9$,[4] and also from the much simpler jellium model[5] for larger sizes. Although the jellium model contains the ingredients to understand the most salient features about alkali-metal-atom clusters[6,7] (it explains, for instance, the magic numbers in the abundance spectrum as due to closed electronic shells), the question of the preferred one among different competing dissociation channels is a delicate one and needs a realistic cluster description. For instance, the spherical jellium model predicts that some $Na_N{}^+$ clusters (N=5,11,12,17,23,24,27,28,29,66–70) in their ground state are unstable against spontaneous dissociation,[5] while it is known from experiment that all $Na_N{}^+$ clusters are stable.[1] This is a consequence of a well-known defect of the spherical jellium model: this model exagerates the amplitude of the oscillations of stability (and of some electronic properties such as the ionization potential) as a function of cluster size.[8] In particular, the stability of alkaline clusters with 8 electrons is overestimated in the jellium model and this extra stability leads to a sizable probability for 8-electron fragments in fission reactions of large clusters, which is not observed in the experiments.[1] When ellipsoidal deformations of the jellium background[9] are allowed, then the stable character of all $Na_N{}^+$ clusters is recovered[10] and the amplitude of the size oscillations of binding energies becomes reduced.

In this paper we consider two improvements of different nature. First, geometrical effects are considered, in an approximate way still easy to handle.[11] Second, instead of the usual local-density approximation (LDA) we employ a more sophisticated nonlocal description of exchange and correlation effects.[12,13] By means of these improvements the energetics and the preferred channels for the dissociation of $Na_N{}^+$ clusters show a clear improvement with respect to the predictions of the standard spherical jellium picture.[5]

II. JELLIUM MODEL

In this and in the following sections we study the dissociation of positively charged Na clusters

$$Na_N{}^+ \rightarrow Na_m + Na_{N-m}{}^+ \tag{1}$$

using different models and approximations and we compare our results with the recent experimental results of Bréchignac *et al.*[1] The heat of dissociation ΔD can be written, in terms of total energies, as

$$\Delta D = E(Na_m) + E(Na_{N-m}{}^+) - E(Na_N{}^+) \ . \tag{2}$$

The jellium model has been used successfully to interpret the main features in the abundance spectrum and some electronic properties of clusters of monovalent metals.[6] In this model the cluster is formed by a homogeneous spherical background of positive charge (representing the ions) with density

$$n_+(\mathbf{r}) = \begin{cases} n_+^0, & r < R \\ 0, & r > R \end{cases}$$

and a distribution of valence electrons (one per atom in the case of a neutral Na cluster) which is calculated self-consistently using the density-functional formalism, with the Hohenberg-Kohn-Sham local-density approximation for exchange and correlation effects.[14,15] The cluster radius R depends on the number of atoms, N. The Gunnarsson-Lundqvist[16] data for the paramagnetic electron gas are used in constructing the LDA.

This model has been used in previous papers[5,17] to study the fragmentation of $Na_N{}^+$ [see Eq. (1)], Na_N, and $Na_N{}^{2+}$ (see also the paper by Rao *et al.*[18]). To be consistent, in those calculations the monomer, Na, is also described by the jellium model. The main conclusion from these works was that the most favorable fragmentation channel (from the point of view of the energy) of neutral or charged Na clusters involves a magic fragment, most often with 2 or 8 electrons (the magic numbers of the jellium model, namely 2,8,18,20, . . . correspond to closed electronic shells). In particular, the preferred channel for the dissociation of $Na_N{}^+$ gives Na_2 or Na_8 as we show in Table I, in the column labeled Jellium (LDA). However, the experiments by Bréchignac *et al.*,[1] reported also in Table I, show that hot $Na_N{}^+$ clusters cool down in most cases by evaporating a neutral monomer (Na), and in a few cases a neutral dimer (Na_2). This clearly indicates that the relative stability of magic clusters is overestimated by the jellium model. Another deficiency of the jellium prediction is that the dissociation of $Na_N{}^+$ is spon-

TABLE I. Most favorable dissociation channel of $Na_N{}^+$ and sign of the corresponding dissociation energy. The preferred channel is indicated by the number m of atoms of the neutral fragment according to reaction $Na_N{}^+ \rightarrow Na_m + Na_{N-m}{}^+$. The sign of the dissociation energy is negative for spontaneous dissociation. The first column gives the number of atoms N in the parent cluster. Then, experimental (Ref. 1) and four sets of theoretical results are given. The columnss labeled Jellium (LDA) and Jellium (NL) have been obtained using the jellium model with local (Ref. 5) and nonlocal descriptions of exchange and correlation effects, respectively. The columns labeled SAPS (LDA) and SAPS (NL) have been obtained using the spherically averaged pseudopotential model with local and nonlocal descriptions of exchange and correlation effects, respectively.

	Expt.		Jellium (LDA)		SAPS (LDA)		Jellium (NL)		SAPS (NL)	
N	m	sign	m	sign	m	sign	m	sign	m	sign
3	1	+	2	+	2	+	1	+	1	+
4	1	+	1	+	1	+	1	−	1	−
5	2	+	2	−	2	−	2	−	2	−
6	1	+	2	+	2	+	2	−	2	+
7	2	+	2	+	1	+	2	+	1	+
8	1	+	2	+	1	+	2	+	1	+
9	1,2	+	1	+	1	+	1	+	1	+
10	1	+	1	+	1	+	1	−	1	+
11	2	+	2	−	2	+	2	−	2	(−)
12	1	+	2	−	2	+	2	−	2	−
13	2	+	2	+	2	+	2	+	2	+
14	1	+	2	+	1	+	2	+	1	+
15	1,2	+	6	+	2	+	2	+	1	+
16	1	+	7	+	7	+	1	+	1	−
17	2	+	8	−	8	+	1	+	2	+
18	1	+	8	+	1	+	1	+	1	+
19	1	+	2	+	1	+	1	+	1	+
20	1	+	1	+	1	+	1	+	1	+
21	1	+	2	+	1	+	2	+	2	+
22			2	+	2	+	2	+	1	+
23	2	+	2	−	2	+	2	−	2	+
24	1	+	2	−	1	+	2	−	1	+
25	1	+	2	+	2	+	2	−	1	+
26	1	+	2	+	17	+	2	+	1	+
27	1	+	8	−	18	+	2	+	1	+
28	1	+	8	−	19	+	2	+	1	+
29	1	+	8	−	20	+	2	+	1	+
30	1	+	8	+	20	+	2	+	1	+
31	1	+	2	+	1	+	2	+	1	+
32	1	+	2	+	1	+	2	+	1	+
33	1	+	2	+	1	+	1	+	1	+
34	1	+	2	+	1	+	1	+	1	+
35	1	+	2	+	1	+	1	+	1	+
36	1	+	2	+	1	+	1	+	1	+
37	1	+	2	+	1	+	2	+	1	+

taneous for some values of N, that is, the heat of dissociation is negative (see Table I), which is contrary to the experimental observations of Bréchignac *et al.*[1] and is linked again to the enhanced stability of magic fragments in the jellium model.

The error introduced by the jellium model in the description of Na_2 is large because the substitution of the two-center system by a jellium sphere is a drastic approximation. The consequence is that the binding energy, E_b, of Na_2 [$E_b(\mathrm{Na}_2)=2E(\mathrm{Na})-E(\mathrm{Na}_2)$] is overestimated: $E_b(\mathrm{Na}_2;\ \text{jellium})=1.50$ eV, whereas the experimental[19] $E_b(\mathrm{Na}_2)$ is 0.75 eV.

We can get an idea of how the overestimated binding of Na_2 affects the fragmentation of $\mathrm{Na}_N{}^+$ by repeating the study described above, using, just for Na_2, the experimental binding energy, whereas all the other clusters are again treated by the jellium model. Then, Table II shows the results of this study, by concentrating in the competition between the two dissociation channels

$$\mathrm{Na}_N{}^+ \rightarrow \mathrm{Na}+\mathrm{Na}_{N-1}{}^+ \tag{3}$$

and

$$\mathrm{Na}_N{}^+ \rightarrow \mathrm{Na}_2+\mathrm{Na}_{N-2}{}^+ \ . \tag{4}$$

The second column of Table II gives the results of the usual jellium model, whereas the third column has been obtained by using the experimental binding energy of Na_2. The evident conclusion is that by lowering the binding of Na_2 the probability of reaction (4) is strongly reduced in favor of an increased probability of reaction (3). This exploratory calculation already gives the clue to the limitations of the jellium model in studying the dissociation of $\mathrm{Na}_N{}^+$. Thus, in the next section we use a model that overcomes some of the main limitations of the jellium model.

TABLE II. Comparison of dissociation channels $\mathrm{Na}_N{}^+ \rightarrow \mathrm{Na}+\mathrm{Na}_{N-1}{}^+$ and $\mathrm{Na}_N{}^+ \rightarrow \mathrm{Na}_2+\mathrm{Na}_{N-2}{}^+$. The most favorable one is indicated by giving the number (1 or 2) of atoms in the neutral fragment. The jellium column is a usual jellium calculation with the LDA approximation. The column labeled (Na_2 expt.) is also a jellium (LDA) calculation but using the experimental binding energy of Na_2 instead of the calculated one.

N	Jellium	Na_2 expt.
3	2	1
4	1	1
5	2	2
6	2	2
7	2	1
8	2	1
9	1	1
10	1	1
11	2	2
12	2	2
13	2	2
14	2	1
15	2	1
16	2	1
17	2	1
18	2	1
19	2	1
20	1	1
21	2	1
22	2	1
23	2	2
24	2	2
25	2	1
26	2	1
27	2	1
28	2	1
29	2	1
30	2	1
31	2	1
32	2	1
33	2	1
34	2	1
35	2	1
36	2	1
37	2	1

III. SPHERICALLY AVERAGED PSEUDOPOTENTIAL MODEL

Theoretical calculations using methods accounting for the granularity of the ions have been performed for very small $\mathrm{Na}_N{}^+$ clusters.[4,20,21] The comparison made by Bréchignac[1] between the experimental dissociation channels and the predictions of those methods for $N \leq 14$ is satisfactory and emphasizes the need to transcend the jellium approximation.

In a previous paper[11] we have introduced a model which goes beyond the jellium model while at the same time it is computationally simple. In this model the geometrical structure of the cluster (at $T=0$ K) is obtained by minimizing the total energy with respect to the positions of all the ions using the density-functional formalism.[14,15] The total energy of the cluster, for a given configuration $\{\mathbf{R}_j\} \equiv \{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_N\}$ of the ions is

$$E[n;\{\mathbf{R}_j\}]=T_s+U_{e\text{-}e}+U_{e\text{-ion}}+U_{\text{ion-ion}}+E_{\text{xc}} \ , \tag{5}$$

where T_s is the single-particle kinetic energy, $U_{e\text{-}e}$ is the classical electron-electron interaction, $U_{e\text{-ion}}$ gives the electron-ion interaction and $U_{\text{ion-ion}}$ the Coulombic ion-ion repulsion. Finally E_{xc} represents the part of the electronic energy due to exchange and correlation effects (treated in the local-density approximation). For a given configuration of the ions $U_{\text{ion-ion}}$ is evaluated immediately and the remaining energies in (5) are obtained in a standard way (see Ref. 15 for details) after self-consistently solving the Kohn-Sham equations (written here in Hartree atomic units)

$$\left[-\frac{\nabla^2}{2}+V_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r}) \ . \tag{6}$$

The effective potential V_{eff} entering the Kohn-Sham equations is the sum of the ion, electron, and exchange-correlation contributions

$$V_{\text{eff}}(\mathbf{r})=V_{\text{ion}}(\mathbf{r})+\int d^3r'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+V_{\text{xc}}(\mathbf{r}) \ , \tag{7}$$

and the ground-state electron density $n(\mathbf{r})$ is evaluated from the occupied single-particle orbitals. The total ionic potential is constructed by adding the pseudopotentials of the individual ions, that is,

$$V_{\rm ion}(\mathbf{r})=\sum_{j} V_{\rm EC}(\mathbf{r}-\mathbf{R}_j)\ , \tag{8}$$

where $V_{\rm EC}(\mathbf{r})$ is the empty-core pseudopotential introduced by Ashcroft.[22] This pseudopotential is zero inside the empty-core radius $r_{\rm EC}$ and Coulombic outside. We take $r_{\rm EC}=1.74$ a.u. With this value the calculated ionization potential of the Na atom is equal to the experimental one.

A drastic approximation is now introduced in order to simplify the computations: the total ionic potential $V_{\rm ion}(\mathbf{r})$ is replaced by its spherical average $V_{\rm ion}^{\rm av}(r)$ about the cluster center. However, we stress that $U_{\text{ion-ion}}$ is evaluated considering the granularity of the ions and is not subject to the spherical averaging. This spherical-average-pseudopotential (SAPS) model is similar in spirit to the spherical-solid model used to treat impurities in bulk solid[23] or liquid[24] metals and is also related to a model used by Manninen[25] in the study of simple metal clusters. In previous papers we have applied the SAPS model to study the binding properties of pure clusters of simple metals[11] and of alloy clusters.[26,27]

A first indication that the SAPS model will lead to a better description of the dissociation of $\mathrm{Na}_N{}^+$ than the jellium model is obtained by calculating the binding energy of Na_2. Even if the effective potential seen by the two valence electrons in the SAPS model is still spherically symmetric around the center of the cluster, the description of the interionic repulsion is treated correctly. The method gives a binding energy $E_b(\mathrm{Na}_2)=0.81$ eV, in very good agreement with the experimental value 0.75 eV. Evidently, this agreement should not be overemphasized.

The most evident improvement is that the sign of the dissociation energy for the most favorable dissociation channel is now given correctly [see the column labeled SAPS (LDA) in Table I and compare with experiment] except for the dissociation of $\mathrm{Na}_5{}^+$, that is, all $\mathrm{Na}_N{}^+$ clusters except $\mathrm{Na}_5{}^+$ are predicted to be stable against spontaneous dissociation. On the other hand, a comparison of the jellium (LDA) and SAPS (LDA) columns of Table I shows that the number of cases in which the evaporation of a monomer is predicted as the most probable dissociation reaction increases from four cases in the jellium model to eighteen in the SAPS model. This is a considerable improvement in the theoretical predictions although there still remain a sizable number of wrong predictions in comparison with the experiment.

Most of the improvement corresponds to cases in which the jellium model predicts reaction (4) as the most favorable one whereas the SAPS model favors reaction (3). On the other hand, there is no significant improvement for clusters in which Na_8 is the preferred fragment in the jellium model:

$$\mathrm{Na}_N{}^+\rightarrow \mathrm{Na}_8+\mathrm{Na}_{N-8}{}^+\ . \tag{9}$$

This is evident for the fragmentation of $\mathrm{Na}_{16}{}^+$, $\mathrm{Na}_{17}{}^+$, and $\mathrm{Na}_{27}{}^+$–$\mathrm{Na}_{30}{}^+$. In these cases (except for $\mathrm{Na}_{30}{}^+$) the SAPS model predicts the following most favorable channel:

$$\mathrm{Na}_N{}^+\rightarrow \mathrm{Na}_{N-9}+\mathrm{Na}_9{}^+\ , \tag{10}$$

in which the (magic) fragment with 8 electrons is now the charged one (in the case of $\mathrm{Na}_{17}{}^+$, both fragments Na_8 and $\mathrm{Na}_9{}^+$ have 8 electrons). This means that the problem of the overestimated stability of the cluster with 8 electrons is not cured by the SAPS model. In the next section we show that a more accurate description of exchange and correlation effects is able to remedy this problem.

IV. INTRODUCTION OF NONLOCAL EFFECTS IN THE EXCHANGE-CORRELATION ENERGY

A. Weighted density approximation

A key ingredient of the Hohenberg-Kohn density-functional theory is the exchange-correlation energy [see Eq. (5)], and the corresponding exchange-correlation potential [see Eq. (7)]. In the usual local-density approximation $V_{\rm xc}(\mathbf{r})$ is determined by the local density $n(\mathbf{r})$ at point $\mathbf{r}$. Although there is ample evidence that the LDA is accurate enough for many purposes in atomic, molecular, and solid-state calculations, there are, nevertheless, problems in which the LDA is not good enough (see for instance the recent paper by Balbás *et al.*[28]). A nonlocal-weighted density approximation (WDA) was proposed some years ago[12,13] with the intention of removing some of the deficiencies of the LDA. The WDA will now be applied in our study of cluster fragmentation. We give here only a brief account of the most salient features of the WDA, referring the reader to our previous paper[28] for more details.

In the density functional theory[15] the exchange-correlation energy of the electrons can be exactly expressed as

$$E_{\rm xc}=\tfrac{1}{2}\int d^3r\, n(\mathbf{r})\int d^3r'\,\frac{n(\mathbf{r}')G(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\ , \tag{11}$$

where $G(\mathbf{r},\mathbf{r}')$ is the pair-correlation function. The exchange-correlation potential $V_{\rm xc}$ is obtained as the functional derivative of $E_{\rm xc}$

$$V_{\rm xc}(\mathbf{r})\equiv\frac{\delta E_{\rm xc}}{\delta n(\mathbf{r})}=V_1(\mathbf{r})+V_2(\mathbf{r})+V_3(\mathbf{r}) \tag{12}$$

with

$$V_1(\mathbf{r})=\tfrac{1}{2}\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}G(\mathbf{r},\mathbf{r}')d^3r'\ , \tag{13a}$$

$$V_2(\mathbf{r})=\tfrac{1}{2}\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}G(\mathbf{r}',\mathbf{r})d^3r'\ , \tag{13b}$$

$$V_3(\mathbf{r})=\tfrac{1}{2}\int\int\frac{n(\mathbf{r}')n(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}\frac{\delta G(\mathbf{r}',\mathbf{r}'')}{\delta n(\mathbf{r})}d^3r'\,d^3r''\ . \tag{13c}$$

The WDA makes the ansatz

$$G(\mathbf{r},\mathbf{r}')=G^{\rm WDA}(|\mathbf{r}-\mathbf{r}'|;\tilde{n}(\mathbf{r}))\ , \tag{14}$$

where $G^{\mathrm{WDA}}(|\mathbf{r}-\mathbf{r}'|;\tilde{n}(\mathbf{r}))$ is the pair correlation function in a homogeneous electron gas of "constant" density n, precisely equal to $\tilde{n}(\mathbf{r})$. The parameter $\tilde{n}(\mathbf{r})$ is fixed at each point $\mathbf{r}$ by requiring the normalization of the exchange-correlation hole for and electron at $\mathbf{r}$

$$\int d^3r'n(\mathbf{r})G^{\mathrm{WDA}}(|\mathbf{r}-\mathbf{r}'|;\tilde{n}(\mathbf{r}))=-1\ . \qquad (15)$$

For the pair-correlation function we use the expression derived by Chacón and Tarazona,[29] which is conveniently given in analytical form.

The exact pair correlation function has the symmetry property $G(\mathbf{r},\mathbf{r}')=G(\mathbf{r}',\mathbf{r})$. This leads to $V_1(\mathbf{r})=V_2(\mathbf{r})$ and then

$$V_{\mathrm{xc}}(\mathbf{r})=2V_1(\mathbf{r})+V_3(\mathbf{r})\ . \qquad (16)$$

For a neutral atom or finite cluster the asymptotic behavior of V_{xc} is then $-1/r$. On the other hand $G^{\mathrm{WDA}}(\mathbf{r},\mathbf{r}';\tilde{n}(\mathbf{r}))$ is nonsymmetric due to the dependence on $\tilde{n}(\mathbf{r})$. The consequence is that $V_1^{\mathrm{WDA}}(\mathbf{r})\neq V_2^{\mathrm{WDA}}(\mathbf{r})$ and that $V_{\mathrm{xc}}^{\mathrm{WDA}}(\mathbf{r})\approx -1/2r$ at large r. This is a significant improvement over the LDA, in which $V_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r})$ decays exponentially at large r. However, the spurious factor of $\frac{1}{2}$ which appears in the WDA still leads to some difficulties, as pointed out in Ref. 28.

A way to remedy this situation was explored in a previous paper,[28] with very promising results. It amounts to forcing the behavior of $V_{\mathrm{xc}}(\mathbf{r})$ embodied in Eq. (16), and thus the correct asymptotic behavior. In this procedure, introduced by Przybylski and Borstel,[30] the exchange-correlation potential is written as

$$V_{\mathrm{xc}}^{\mathrm{PB}}(\mathbf{r})=2V_1^{\mathrm{WDA}}(\mathbf{r})+V_3^{\mathrm{WDA}}(\mathbf{r})\ . \qquad (17)$$

After the Kohn-Sham equations have been solved with the use of $V_{\mathrm{xc}}^{\mathrm{PB}}$, then the total energy is computed in the usual way, employing $E_{\mathrm{xc}}^{\mathrm{WDA}}$ as the exchange-correlation energy functional. The price paid for the improvement in V_{xc} is that $V_{\mathrm{xc}}^{\mathrm{PB}}$ is not the functional derivative of $E_{\mathrm{xc}}^{\mathrm{WDA}}$, so the method is not fully self-consistent. There still remains the very difficult task of finding the exchange-correlation energy functional that, by functional differentiation [see Eq. (12)], leads to $E_{\mathrm{xc}}^{\mathrm{PB}}$. This unknown functional, if expressed in the form given in Eq. (11) must be based on a pair correlation function showing the proper symmetry between $\mathbf{r}$ and $\mathbf{r}'$.

B. Results for the jellium model

Calculations, within the jellium-model framework, but using the nonlocal WDA description of exchange and correlation effects, have been performed to study the dissociation of $\mathrm{Na}_N{}^+$. The results for the most favorable dissociation channel and for the sign of the heat of the reaction are given in Table I in the columns under the label Jellium (NL). These results should now be compared with those obtained within the same jellium model using the LDA.

The main observation is that the problem concerning fragments with 8 electrons has been solved by virtue of the nonlocal description of exchange and correlation. The dissociation through reactions (9) and (10) has been completely eliminated in favor of reactions (3) and (4). This is explained by a lowering of the stability of Na_8, as it can be observed by looking at Fig. 1, where the cohesive energy per atom of Na_N is plotted versus N. The cohesive energy per atom is defined

$$E_c(\mathrm{Na}_N)=E\ (\mathrm{Na})-\frac{1}{N}E(\mathrm{Na}_N)\ . \qquad (18)$$

The nonlocal calculation gives a lower cohesion than the LDA calculation. Although this lowering of cohesion affects all clusters, the effect is particularly strong around Na_8. Notice that E_c (Na_8) is larger than E_c (Na_2) in the LDA but smaller than E_c (Na_2) in the nonlocal calculation. The electronic configuration of Na_8 is $(1s)^2(1p)^6$ and $1d$ is the first unoccupied level. Then the magnitude of the gap between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) gives evidence for the reduction in the shell-closing stabilization effect. $\varepsilon(1d)-\varepsilon(1p)$ equals 1.48 eV in the LDA, and 1.27 eV in the nonlocal calculation; that is, the HOMO-LUMO gap has been decreased by 15% by the introduction of nonlocal exchange-correlation effects.

The universal lowering of binding strength enhances the probability of reaction (3); this is also observed in Table I. Preliminary calculations suggest that E_c grows fast for $N>37$ in the nonlocal calculation, and that the predicted bulk limit will not differ much from the LDA bulk limit.

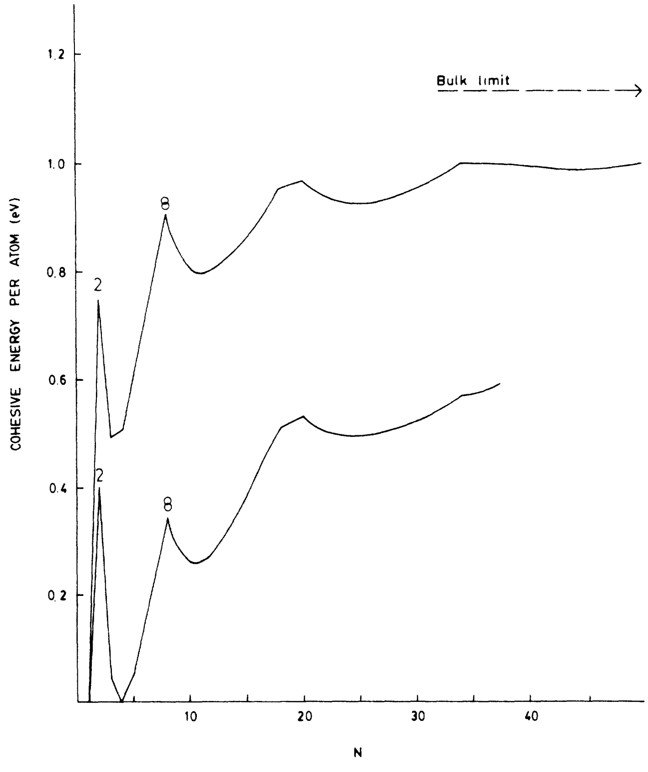

FIG. 1. Cohesive energy per atom, $E_c(\mathrm{Na}_N)=E(\mathrm{Na})-(1/N)E(\mathrm{Na}_N)$, vs cluster size calculated within the jellium model. The upper curve is for the local density approximation for exchange and correlation and the lower curve for the nonlocal WDA. The experimental bulk limit is indicated.

C. Results for SAPS model

Finally we report results obtained for the SAPS model (see Sec. III above) in conjunction with the nonlocal description of exchange and correlation. These results are given in Table I under the label SAPS (NL). With respect to the most favorable dissociation reaction we obtain very satisfactory predictions. Most Na_N^+ clusters dissociate according to reaction (3), that is, emitting a neutral monomer, and only a few clusters emit a neutral dimer. Compared to experiment the theoretical prediction makes just four errors (corresponding to the dissociation of Na_6^+, Na_7^+, Na_{12}^+, and Na_{21}^+), which is a very substantial improvement with respect to our previous paper[5] where we used the jellium model and the local-density approximation [see the jellium (LDA) column of Table I].

Figure 2 gives the heat of dissociation ΔD for the most favorable reaction, which is compared to the experimental values measured by Bréchignac *et al.*[1] The experimental ΔD shows pronounced maxima for $N=3$ and 9. The reason is that Na_3^+ and Na_9^+ are very stable closed-shell clusters, with 2 and 8 electrons, respectively. These two maxima are reproduced by the calculation. Several other experimental maxima of lower magnitude, such as those at $N=13$, 15, and 19, are also reproduced by the calculation (Na_{19}^+ is also a closed-shells cluster). The calculation, nevertheless, exaggerates the amplitude of the oscillations of ΔD with cluster size. This is, no doubt, a consequence of the fact that the SAPS model still has a tendency to exaggerate the electronic shell effects. Correction of this deficiency evidently needs a better cluster model,[4,20] avoiding the spherical average of the total ionic potential. But this, then, imposes severe limitations on the size of the clusters that can be handled.[4,18,20,21]

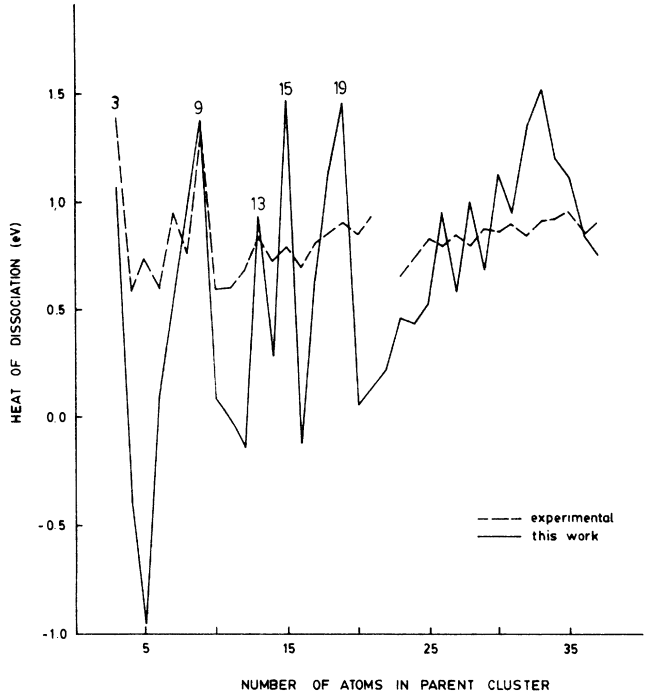

FIG. 2. Energy balance for the most favorable dissociation reaction of Na_N^+, vs N. Experimental results are from Bréchignac *et al.* (Ref. 1). Calculated results use the SAPS model and the nonlocal description of exchange and correlation.

V. SUMMARY

The dissociation of Na_N^+ clusters has been studied using the density functional theory.

(1) The use of the jellium model and the usual local-density approximation for exchange and correlation effects leads to a dissociation behavior dominated by a strong tendency to give fragments with closed electronic shells, mainly Na_2, Na_8, and Na_9^+. Instead, the experiments of Bréchignac and co-workers[1] indicate that most clusters dissociate by evaporating a neutral monomer (Na), and in a few cases a neutral dimer (Na_2). Monomer evaporation is also confirmed by a recent experimental study of K_N^+ clusters.[31]

(2) The jellium model overestimates the binding of Na_2 by a factor of 2 compared to experiment. We have then used an improved model (SAPS model) which corrects this deficiency, leading to an enhanced number of dissociations through the monomer channel. In the improved model the ion-ion interactions are accounted for correctly, but the valence electrons interact with the spherically averaged ionic pseudopotential (averaged about the cluster center).

(3) Still the SAPS model is unable to eliminate the fragmentations in which the 8-electron cluster is involved. A nonlocal description of exchange and correlation effects (weighted density approximation) reveals that the problem of the enhanced stability of the 8-electron cluster can be corrected. Finally the simultaneous use of the SAPS model and the weighted density approximation leads to a dissociation behavior in good agreement with experiment. The calculated dissociation energy shows the main features observed in the measured one, but the size oscillations of the dissociation energy are overestimated in the theoretical calculation. This would need a more refined cluster model, which is not a trivial task for large size clusters.

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