

Convergence from clusters to the bulk solid: an *ab initio* investigation of clusters Na_nCl_n ($n = 2\text{--}40$)

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Paper

The electronic structures of a series of sodium chloride clusters $(\text{NaCl})_n$ ($n = 2\text{--}40$) cut out from the NaCl solid have been investigated by means of *ab initio* calculations. The calculation results demonstrated a good correlation of the topologic parameters N_d (the total amount of dangling bonds of a cut-out cluster) and β (the average dangling bonds on each in-cluster atom) with the stability of clusters as well as an evident convergence from clusters to the bulk solid. Particularly, we found that the effective charges on the Cl anions are more site dependent than size dependent.

I. Introduction

Clusters are intermediates in the transition between gaseous and condensed phases that make them an attractive and valuable subject of experimental and theoretical investigation of the emergence of condensed-matter properties. On the other hand, the cluster approach has been widely employed to study the properties of bulk solids and the chemisorptions and reactions on solid surfaces, and many successful applications have been made in the recent years.^{1–20} On both accounts, an important question is to what extent a cluster consisting of only a few atoms behaves like a respective bulk solid. To look for the answer to this question, much effort has been made by both experimentalists and theoreticians in the past decades. Some basic rules to justify the cluster approach and to guarantee a reasonable cluster modeling have been proposed by theoreticians. For example, for the cluster modeling of an ionic solid, a reasonable cluster model should at least fulfill the following principles, *i.e.*, neutrality principle, stoichiometry principle and coordination principle. The reliability of these practical principles has been verified previously in the *ab initio* studies on the $(\text{MgO})_x$ ($x = 2\text{--}16$) and $(\text{ZnO})_x$ ($x = 3\text{--}13$) clusters.^{1–3} In the present work, we deal systematically with the structures and electronic properties of stoichiometric clusters Na_nCl_n for n up to 40. The main purpose of our study is to determine the cluster properties over a sufficient range of n to ascertain the convergence – *e.g.* of charge, structure, bond distances, binding energy – towards bulk solid properties.

In the course of the study on the cluster–solid similarity, alkali halide clusters have been widely studied due to its structural simplicity.^{4–12} Based on SIMS (secondary ion mass spectroscopy) and other mass spectroscopic probes,^{21,22} which show stability islands among the alkali halide cluster cations corresponding to closed segments of the bulk lattice, it has been generally assumed that even quite small alkali halide clusters maintain the global features of bulk-like structure and ionic bonding. This view has been supported by theoretical calculations ranging in different sophistication.^{1–13} *Ab initio* investigations of clusters Na_nCl_n and K_nCl_n ($n = 1\text{--}32$) by Ochsenfeld *et al.*^{4–7} revealed that the energetically most stable isomers of even smaller clusters show a clear preference for geometries which are fragments of the solid state lattice. Similar preference has also been found by Ayuela *et al.*,^{8–13} using the *ab initio* perturbed-ion (PI) model, which is formulated within the restricted Hartree–Fock (RHF) approximation,

in studies of neutral stoichiometric alkali halide^{8–12} and $(\text{MgO})_n$ clusters.¹³ In their semi-empirical SINDO1 study of the $(\text{NaCl})_x$ ($16 \leq x \leq 168$) clusters, Jug and Geudtner¹⁹ established a quasilinear relationship between normalized binding energies or average bond distances and relative average coordination numbers. In our previous paper, we proposed three practical rules, *i.e.*, neutrality principle, stoichiometry principle and coordination principle, for a better cluster modeling of ionic solid and justified these rules by case studies on a series of $(\text{ZnO})_n$ ($n = 3\text{--}13$)¹ and $(\text{MgO})_n$ ($n = 2\text{--}16$)^{2,3} clusters. A good correlation of the stability of the metal oxide clusters with the topological parameters N_d (the total amount of dangling bonds of a cut-out cluster) and β (the average dangling bonds on each in-cluster atom) were found in these case studies. In the present work, these three principles are applied to the cluster modeling of NaCl solid and, accordingly, *ab initio* calculations on a series of $(\text{NaCl})_n$ ($n = 2\text{--}40$) clusters have been performed. The size effect, as well as the site effect, of the clusters to the structures and electronic properties has been investigated systematically.

II. Details of computation

As a typical ionic-bonding crystal, the sodium chloride crystal has a rock-salt (cubic) structure where each bulk Na or Cl ion is coordinated by six counterions respectively and the measured interionic distance ($d_{\text{Na-Cl}}$) is 2.814 Å.²³ In the present work, a series of neutral, stoichiometric $(\text{NaCl})_n$ ($n = 2\text{--}40$) clusters whose geometries are cut out from the bulk solid have been systematically investigated.

Various methods and basis sets have been used to calculate the structures and electronic properties of $(\text{NaCl})_n$ clusters. Since sodium chloride solid is generally believed to be highly ionic, the ground states of these $(\text{NaCl})_n$ clusters considered were supposed to be in closed shells. In this way, the restricted Hartree–Fock (RHF) method has been safely employed. As alkali halides clusters are ideal candidates for an application of the ECP (effective core potential) approximation,²⁴ we have used CEP-31G*,²⁵ which paves the way for an efficient treatment of the larger clusters, as the basis sets for Na and Cl atoms. In addition, the possibility of correlation effects has been investigated by B3LYP,^{26,27} the applicability of which to ionic systems has been validated, for example, in a recent theoretical study on $(\text{MgO})_n$ ($n = 1\text{--}16$) and $(\text{CaO})_n$ ($n = 1\text{--}12$)

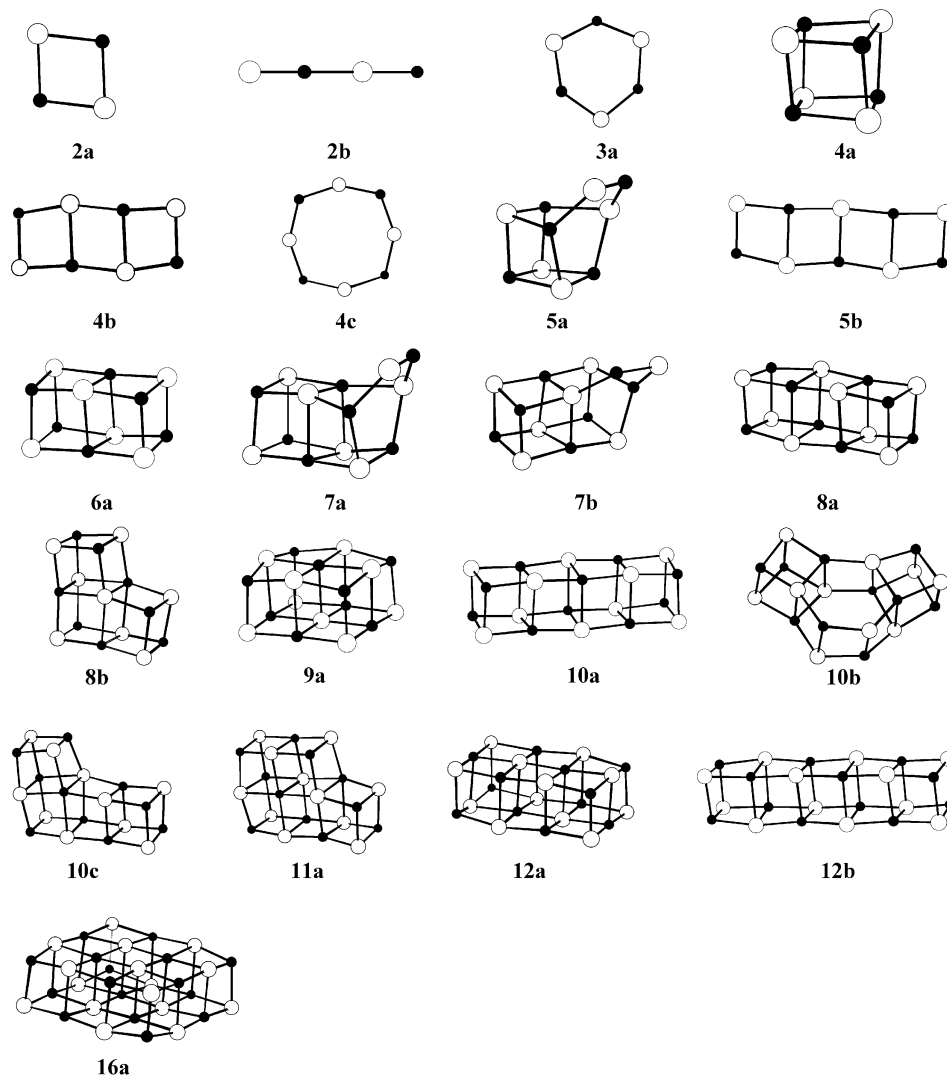


Fig. 1 Geometries of the $(\text{NaCl})_n$ ($n = 2-16$) clusters.

clusters²⁰ by comparing the B3LYP predictions with the reference calculations at the MP2 and MP4 levels of theory^{28,29} and experimental results. What is more, to test the reliability of the effective core potential approximation, larger basis sets, *i.e.*, the standard 6-31G* for RHF method and 6-311G* for B3LYP method, have been employed. All calculations were performed with the Gaussian98 package.³⁰

III. Results and discussion

III.A. Structures and electronic properties of $(\text{NaCl})_n$ clusters

The calculated structures of $(\text{NaCl})_n$ clusters are shown in Fig. 1 where small spheres represent cations and large spheres represent anions. It should be noted that there are a number of different choices to cut out a cluster for a given cluster size n from the perfect NaCl solid, in which every Na or Cl atom is six-fold coordinated, and such procedure will inevitably give border atoms of lower coordination numbers. On this account, N_d and β ,¹ which are related to the coordination number κ ,¹⁹ can be easily established. Table 1 presents the calculated properties of $(\text{NaCl})_n$ clusters, including NaCl-unit RHF energy (*i.e.* RHF/ n), bond distance, cluster dissociation energy to ions, average Mulliken charge, NaCl removal energy and cluster atomization energy.

Table 1 Electronic properties of $(\text{NaCl})_n$ ($n = 2-16$) clusters calculated at RHF/CEP-31G* level

Cluster	Symmetry	N_d	β	$E/n / E_h$	$\Delta_a^{(n)}/\text{eV}^a$	$\Delta^{(n)}(\text{NaCl})/\text{eV}^b$
2a	D_{2h}	16	4.0	-14.980443	7.88	2.10
2b	C_{2v}	18	4.5	-14.962430	6.89	1.12
3a	C_{2v}	22	3.67	-14.990744	12.64	1.89
4a	T_d	24	3.0	-15.000390	17.91	2.38
4b	C_{2h}	28	3.5	-14.993894	17.20	1.67
4c	C_{2v}	32	4.0	-14.993655	17.17	1.65
5a	C_1	30	3.0	-14.999643	22.28	1.49
5b	C_{2v}	34	3.4	-14.996573	21.86	1.07
6a	D_{2h}	32	2.67	-15.004843	27.58	2.42
7a	C_1	38	2.71	-15.004750	32.16	1.70
7b	C_1	38	2.71	-15.003708	31.97	1.50
8a	D_{2d}	40	2.5	-15.008158	37.50	2.45
8b	C_s	40	2.5	-15.006761	37.20	2.15
9a	C_{4v}	42	2.33	-15.009455	42.51	2.12
10a	D_{2h}	48	2.4	-15.009652	47.28	1.89
10b	C_2	48	2.4	-15.008798	47.05	1.66
10c	C_1	48	2.4	-15.008682	47.02	1.63
11a	C_1	50	2.27	-15.009736	52.04	1.87
12a	C_{2h}	52	2.17	-15.011615	57.38	2.46
12b	D_{2d}	56	2.33	-15.010651	57.07	2.15
16a	D_{2d}	64	2.0	-15.013514	77.34	

^aCluster atomization energy $\Delta_a^{(n)} = nE(\text{Cl}) + nE(\text{Na}) - E((\text{NaCl})_n)$.
^bNaCl removal energy $\Delta^{(n)}(\text{NaCl}) = E((\text{NaCl})_{n-1}) + E(\text{NaCl}) - E((\text{NaCl})_n)$.

Some interesting properties of the $(\text{NaCl})_n$ clusters can be seen from Fig. 1 and Table 1. These are:

1. The cluster, *e.g.*, (2a), (3a), (4a), (5a), (6a), (7a), (8a), (9a), (10a), (11a), (12a) and (16a), having the least dangling bonds (the smallest N_d) is the most stable (having the lowest NaCl-unit energy) among those of the same size. Such result may be due to the well-known edge effect. For a given cluster size n , the cluster, which has minimum N_d (or the highest coordination number), should have the smallest edge effect and should be the most stable. The present result fully supports the quite popular model^{14,31–33} that $(\text{NaCl})_n$ clusters preferably occur as $k \times l \times m$ (with $km = 2n$) fragments of the solid, especially when $k = l = m$. In other words, $(\text{NaCl})_n$ clusters prefer densely packed structures as in the solid.

2. Compared to the other clusters, those clusters, as for $(\text{NaCl})_2$, $(\text{NaCl})_3$, $(\text{NaCl})_5$ and $(\text{NaCl})_7$, where no densely packed structure like in the bulk lattice is possible have reduced stability. Such a result can be easily explained by using the topological parameter N_d . To maintain a low N_d , cluster atoms with coordination number smaller than 3 should be avoided. Actually, no atoms coordinated with fewer than three counterions exist in the real NaCl solid, while cluster atoms with coordination numbers of fewer than three are unavoidable for those clusters whose sizes are 2, 3, 5 and 7. Owing to the presence of the lower coordinated cluster atoms, those clusters are unstable with higher NaCl-unit energy. As a consequence, this kind of cluster would not offer a good model of NaCl solid. In this way, it provides a simple but efficient means to exclude some cluster models from detailed consideration.

3. Along with the increase of n , there are more and more inner atoms that are fully coordinated, the corresponding β decreases and the cluster becomes more stable. In other words, the largest β corresponds to the highest NaCl-unit energy, while the smallest β corresponds to the lowest NaCl-unit energy, evidencing that the topological parameter β can be a measurement of the relative stability of the clusters of different size.

4. For those clusters with the same N_d , *e.g.*, (8a, 8b) or (10a, 10b, 10c), the one with higher symmetry is more stable with lower NaCl-unit energy. This clearly demonstrates that the edge effect could be further divided into two effects, *i.e.*, the size effect (dependent on the size of the cluster) and the shape effect (dependent on the shape of the cluster). In this regard, the topological parameters N_d and β provide a way to keep the shape effect under control.

5. The energy required to remove a NaCl molecule from the cluster ($\Delta_1^{(n)}(\text{NaCl}) = E((\text{NaCl})_{n-1}) - E((\text{NaCl})_n)$) is larger

for clusters (4a), (6a), (8a), (12a) while it is interesting to see that there is a destroy of the cubic-like structure from $(\text{NaCl})_n$ to $(\text{NaCl})_{n-1}$ ($n = 4a, 6a, 8a, 12a$). On this account, the non-monotonic variation of $\Delta_1^{(n)}(\text{NaCl})$ with n may be correlated with such a change; *i.e.* removing a NaCl molecule from $(\text{NaCl})_n$ to form $(\text{NaCl})_{n-1}$ (that is, $\Delta_1^{(n)}(\text{NaCl})$) when $(\text{NaCl})_n$ is 4a, 6a, 8a or 12a involves a transformation from a cubic-like structure to form a non-cubic one. On the other hand, the other smaller values of $\Delta_1^{(n)}(\text{NaCl})$ are just associated with transformations between two cubic-like clusters or non-cubic clusters. Such a trend demonstrates that densely packed structures like fragments of the solid-state f.c.c. lattice are favored.

III.B. Convergence from the clusters to the bulk solid

It is of particular importance to investigate the convergence of the calculated structural and electronic properties of a cut out cluster with the increase of cluster size. However, from Table 1, it is hard to draw a clear conclusion if the shapes of the clusters are chosen arbitrarily. We then focus on the $(\text{NaCl})_n$ ($n = 4a, 6a, 8a, 9a, 12a, 16a$) clusters, believing that the set of clusters with smallest N_d of each given size provides a suitable starting point to study the cluster size dependence of the computed properties since the shape effect is under control. From Table 2 and Fig. 2, interesting convergence, based on the NaCl-unit energy, bond distance, binding energy, as well as the effective charges in Cl atom, for this specific set of $(\text{NaCl})_n$ clusters has been shown.

1. The NaCl-unit energy of a cluster decreases monotonously with the increase of the cluster size (see Fig. 2), while the NaCl-unit energies of those clusters in arbitrary shapes oscillate. The more severely the shapes differ, the larger the oscillation (see Table 1).

2. The average distance between neighboring alkali and halogen atom, *i.e.*, $d_{\text{Na-Cl}}$, increases with the cluster size n . In clusters (4a), (6a), (8a), (9a) and (12a), $d_{\text{Na-Cl}}$ is 2.701, 2.728, 2.738, 2.758 and 2.766 Å, respectively. We note that in cluster (16a) $d_{\text{Na-Cl}}$ is 2.776 Å, which is similar to the measured interionic distance in the bulk cubic crystal, 2.814 Å²³ and to the predicted values around 2.90 Å by periodic HF calculations.^{34,35} The increasing Na–Cl distance could be a hint of the increasing ionicity of the in-cluster atoms.

3. With the cluster size n increases, there are more and more high coordinated atoms and the effect of the ionic binding must be stronger. As a consequence, the binding energy per ion-pair also increases. Thus we note that the binding energy per ion-pair ($\Delta_1^{(n)}/n$, from Table 1) increases monotonically, starting

Table 2 Convergence of the structural and electronic properties of $(\text{NaCl})_n$ ($n = 4-16$) clusters calculated at RHF/CEP-31G* level as well as the theoretical and experimental bulk values available

Cluster	$\Delta_1^{(n)}$ (eV) ^a	$\Delta_d^{(n)}$ /eV ^b	$\Delta_b^{(n)}$ /eV ^c	$d_{\text{Na-Cl}}$ /Å	Q_0^d	Q^e
4a	28.99	6.37	7.25	2.701	3c: -0.635	-0.635
6a	44.22	10.29	7.37	2.728	3c: -0.630 4c: -0.667	-0.642
8a	59.68	14.44	7.46	2.738	3c: -0.632 4c: -0.678	-0.655
9a	67.45	16.56	7.49	2.758	3c: -0.641 4c: -0.681 5c: -0.703	-0.666
12a	90.64	22.79	7.55	2.766	3c: -0.636 4c: -0.683 5c: -0.711	-0.672
16a	121.68	31.21	7.61	2.776	3c: -0.633 4c: -0.685 5c: -0.717	-0.680
Bulk HF			7.64 ^f	2.90 ^f , 2.89 ^g		-0.985 ^g
Expt			7.98 ^h	2.814 ⁱ		

^aCluster dissociation energy to ions $\Delta_1^{(n)} = nE(\text{Cl}^-) + nE(\text{Na}^+) - E((\text{NaCl})_n)$. ^bCluster dissociation energy to NaCl $\Delta_d^{(n)} = nE(\text{NaCl}) - E((\text{NaCl})_n)$. ^cBinding energy $\Delta_b^{(n)} = \Delta_1^{(n)}/n = E(\text{Cl}^-) + E(\text{Na}^+) - E((\text{NaCl})_n)/n$. ^dMulliken charges Q_0 for different fold coordinated Cl atoms. ^eAverage Mulliken charges Q for all inner Cl atoms. ^fRef. 34. ^gRef. 35. ^hRef. 36. ⁱRef. 23.

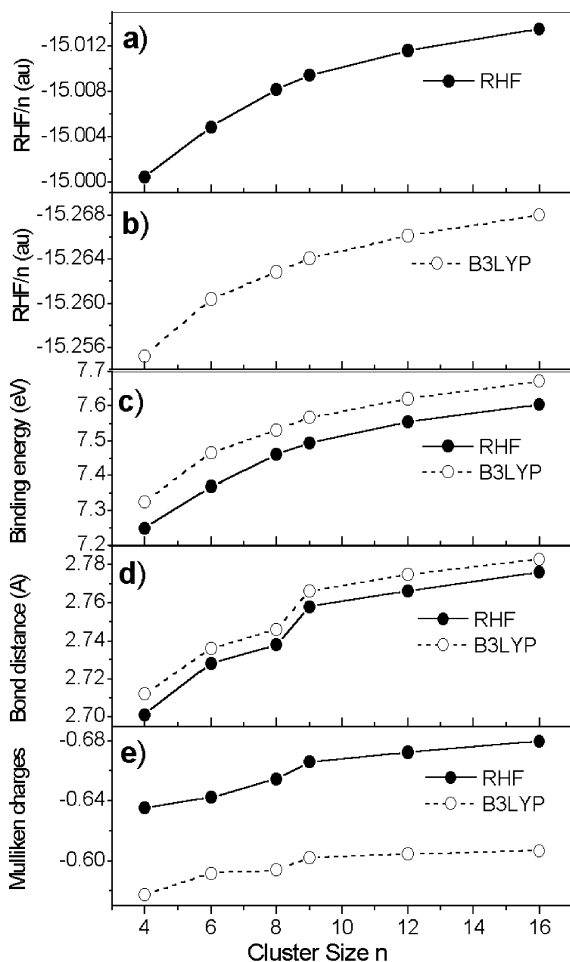


Fig. 2 Convergence of the structural and electronic properties of $(\text{NaCl})_n$ ($n = 4a, 6a, 8a, 9a, 12a, 16a$) clusters. (a) RHF/ n (RHF calculation); (b) RHF/ n (B3LYP calculation); (c) binding energy $\Delta_b^{(n)} = \Delta_1^{(n)}/n = E(\text{Cl}^-) + E(\text{Na}^+) - E((\text{NaCl})_n)/n$; (d) bond distance $d_{\text{Na-Cl}}$; (e) average Mulliken charges Q for all inner Cl atoms.

from 7.25 eV for the cluster (4a) and through 7.37, 7.46, 7.49, 7.55 and 7.61 eV for cluster (6a), (8a), (9a), (12a) and (16a), respectively, and approaching the measured lattice energy of 7.98 eV of bulk solid,³⁶ and the predicted lattice energy of 7.64 eV by periodic HF calculation.³⁴

4. Although the atomic charges depend largely on the model used to calculate them and they are not physically observable as well, it is still of great interest to investigate the convergence of atomic charges. As a typical ionic-bonding crystal, sodium

chloride solid is highly ionic. It is natural for one to expect that with the increase of cluster size n , the magnitude of the in-cluster atomic charges will also increase and will approach to the bulk value, which should be around the formal charge ± 1 ,³⁵ in the long run. From Table 2 and Fig. 2, it has been shown that although the atomic charges in clusters $(\text{NaCl})_n$ differ significantly from the formal charge ± 1 , they increase in magnitude as n increases. Similar trend has been found in $(\text{MgO})_n$ ($n < 4$) by Bilydyrev *et al.*³⁷ However, through careful inspection of the calculated charges (see Table 2), we may find that by keeping the clusters in the same shape, the atomic charges show not only size dependence, but also noteworthy site dependence, similar to the $(\text{MgO})_n$ case.^{2,37,38} That is, the average Mulliken charges of Cl atoms increase with the increase of the cluster size n , while for any given fold coordinated Cl atoms the magnitude of the Mulliken charges are always around a constant regardless of the size of the clusters. For instance, the Mulliken charges for the three-fold coordinated Cl atoms are always around -0.63 , while the Mulliken charges for the four-fold and five-fold coordinated Cl atoms are always around -0.68 and -0.71 , respectively. On the other hand, along with the increase of n , there are more and more inner atoms and the percent of the higher fold coordinated atoms also increases. As a consequence, the average charge of the in-cluster atoms increases with the increase of the cluster size. Thus we find the average Mulliken charges of anions in clusters (4a), (6a) and (8a) are -0.635 , -0.642 and -0.655 , respectively, while those of (9a), (12a) and (16a) are -0.666 , -0.672 and -0.680 , respectively.

Furthermore, such convergence has also been investigated by means of B3LYP method, which is a hybrid method including a mixture of the HF exchange with the DFT exchange-correlation. The results that incorporate the correlation effects have been shown in Table 3 and Fig. 2. From the comparisons to those from the HF calculations, we have found the same convergence as that we get from the HF calculations. Again we found that the NaCl-unit energies decrease monotonously with the increase of cluster size for the set of clusters with the fewest dangling bonds.

The B3LYP-predicted bond distance also increases with the increasing of cluster size n , identical to the trend predicted by HF calculations. However, the incorporation of electron correlation leads to a longer Na–Cl distance. For example, the B3LYP predicted $d_{\text{Na-Cl}}$ of (2a) is 2.626 Å compared to the HF value of 2.620 Å, whereas the B3LYP bond distance of (16a) is 2.783 Å compared to the HF value of 2.776 Å. It is noteworthy that both the RHF and B3LYP predicted bond distances for the $(\text{NaCl})_2$ cluster (2a) agree well with the experimental value of 2.584 ± 0.034 Å³⁹ measured for the gas-phase $(\text{NaCl})_2$

Table 3 Convergence of the structural and electronic properties of $(\text{NaCl})_n$ ($n = 4-16$) clusters calculated at B3LYP/CEP-31G* level

Cluster	$E/n / E_h$	$\Delta_1^{(n)}/\text{eV}^a$	$\Delta_d^{(n)}/\text{eV}^b$	$\Delta_b^{(n)}/\text{eV}^c$	$d_{\text{Na-Cl}}/\text{Å}$	Q_0^d	Q^e
4a	-15.255228	29.30	6.18	7.32	2.712	3c: -0.578	-0.578
6a	-15.260401	44.79	10.11	7.47	2.736	3c: -0.583 4c: -0.608	-0.592
8a	-15.262836	60.25	14.01	7.53	2.746	3c: -0.578 4c: -0.609	-0.594
9a	-15.264107	68.10	16.07	7.57	2.766	3c: -0.585 4c: -0.614 5c: -0.620	-0.602
12a	-15.266156	91.47	22.10	7.62	2.775	3c: -0.580 4c: -0.614 5c: -0.624	-0.604
16a	-15.267986	122.75	30.26	7.67	2.783	3c: -0.576 4c: -0.613 5c: -0.625	-0.607

^aCluster dissociation energy to ions $\Delta_1^{(n)} = nE(\text{Cl}^-) + nE(\text{Na}^+) - E((\text{NaCl})_n)$. ^bCluster dissociation energy to NaCl $\Delta_d^{(n)} = nE(\text{NaCl}) - E((\text{NaCl})_n)$. ^cBinding energy $\Delta_b^{(n)} = \Delta_1^{(n)}/n = E(\text{Cl}^-) + E(\text{Na}^+) - E((\text{NaCl})_n)/n$. ^dMulliken charges Q_0 for different fold coordinated Cl atoms. ^eAverage Mulliken charges Q for all inner Cl atoms.

Table 4 Mulliken charges of $(\text{NaCl})_n$ ($n = 4-40$) clusters single-point calculated at RHF/CEP-31G* and B3LYP/CEP-31G* levels

Cluster	RHF/CEP-31G*		B3LYP/CEP-31G*	
	Q_0^a	Q^b	Q_0	Q
4a ($2 \times 2 \times 2$)	3c: -0.680	-0.680	3c: -0.619	-0.619
6a ($3 \times 2 \times 2$)	3c: -0.681	-0.687	3c: -0.620	-0.622
	4c: -0.698		4c: -0.627	
8a ($4 \times 2 \times 2$)	3c: -0.679	-0.689	3c: -0.617	-0.621
	4c: -0.699		4c: -0.626	
9a ($3 \times 3 \times 2$)	3c: -0.680	-0.695	3c: -0.616	-0.623
	4c: -0.705		4c: -0.627	
	5c: -0.716		5c: -0.630	
12a ($4 \times 3 \times 2$)	3c: -0.678	-0.698	3c: -0.613	-0.623
	4c: -0.704		4c: -0.627	
	5c: -0.721		5c: -0.630	
16a ($4 \times 4 \times 2$)	3c: -0.676	-0.702	3c: -0.612	-0.624
	4c: -0.704		4c: -0.628	
	5c: -0.725		5c: -0.630	
24 ($4 \times 4 \times 3$)	3c: -0.676	-0.715	3c: -0.610	-0.630
	4c: -0.707		4c: -0.629	
	5c: -0.732		5c: -0.637	
	6c: -0.767		6c: -0.644	
32 ($4 \times 4 \times 4$)	3c: -0.674	-0.722	3c: -0.606	-0.627
	4c: -0.707		4c: -0.626	
	5c: -0.734		5c: -0.632	
	6c: -0.776		6c: -0.637	
40 ($4 \times 4 \times 5$)	3c: -0.673	-0.724	3c: -0.606	-0.630
	4c: -0.706		4c: -0.626	
	5c: -0.734		5c: -0.635	
	6c: -0.773		6c: -0.644	

^aMulliken charges Q_0 for different fold coordinated Cl atoms. ^bAverage Mulliken charges Q for all inner Cl atoms.

cluster. Such agreement demonstrates the applicability of the B3LYP functional to ionic systems such as NaCl.

Generally speaking, the atomic charges are sensitive to the methods and basis sets employed and the inclusion of correlation effects seemly tends to decrease the magnitude of the atomic charges. From Table 2, Table 3 and Fig. 2, it can be seen that the magnitudes of the B3LYP-predicted atomic charges are constantly smaller than the corresponding HF

ones. In spite of that, it is still true that the atomic charges are more site dependent than size dependent. For instance, the Mulliken charges for the three-fold, four-fold and five-fold coordinated Cl atoms are always around -0.58, -0.61 and -0.62, respectively, while the average magnitude of the Mulliken charges increases with the increase of the cluster size n , stating from -0.578 for (4a) to -0.607 for (16a).

Seeing that the clusters favor the densely packed structures, we have employed single-point calculation for $(\text{NaCl})_n$ ($n = 4-40$), which are cubic with the nearest Na-Cl distance being fixed to the bulk value of 2.814 Å, to investigate the convergence of the larger clusters. The results are shown in Table 4. In the single-point HF calculations, the Mulliken charges for the three-fold, four-fold, five-fold and six-fold coordinated Cl atoms are always around -0.68, -0.70, -0.73 and -0.77, respectively, while the average Mulliken charges increase monotonously with the increase of the cluster size, from -0.680 for $(\text{NaCl})_4$ ($2 \times 2 \times 2$) to -0.724 for $(\text{NaCl})_{40}$ ($4 \times 4 \times 5$). In the single-point B3LYP calculations, the Mulliken charges of the three-fold, four-fold, five-fold and six-fold coordinated Cl atoms are always about -0.61, -0.63, -0.63 and -0.64, respectively, whereas the average Mulliken charge increases from -0.578 for $(\text{NaCl})_4$ ($2 \times 2 \times 2$) to -0.730 for $(\text{NaCl})_{40}$ ($4 \times 4 \times 5$).

III. Basis set effects

To test the reliability of the effective core potential approximation, larger basis sets, *i.e.*, the standard 6-31G* for RHF calculations and 6-311G* for B3LYP calculations, have been employed. The results are given in Table 5 and Table 6, respectively, which are roughly the same as those obtained by using the CEP-31G* basis set.

IV. Conclusion

The structure and electronic properties of a series of sodium chloride clusters $(\text{NaCl})_n$ ($n = 2-40$) have been investigated by means of the *ab initio* method. The main results are:

- (i) Whenever possible, densely packed structures like

Table 5 RHF calculations for $(\text{NaCl})_n$ ($n = 4, 6, 8, 9$) clusters with 6-31G* basis sets

Cluster	$E/n / E_h$	$\Delta_1^{(n)}/\text{eV}^a$	$\Delta_d^{(n)}/\text{eV}^b$	$\Delta_b^{(n)}/\text{eV}^c$	Q_0^d	Q^e
4a	-621.456437	29.51	6.18	7.38	3c: -0.685	-0.685
6a	-621.461069	45.03	10.03	7.50	3c: -0.684	-0.698
					4c: -0.725	
8a	-621.463501	60.56	13.91	7.57	3c: -0.682	-0.705
					4c: -0.727	
9a	-621.464784	68.45	15.96	7.61	3c: -0.686	-0.713
					4c: -0.726	
					5c: -0.771	

^aCluster dissociation energy to ions $\Delta_1^{(n)} = nE(\text{Cl}^-) + nE(\text{Na}^+) - E((\text{NaCl})_n)$. ^bCluster dissociation energy to NaCl $\Delta_d^{(n)} = nE(\text{NaCl}) - E((\text{NaCl})_n)$. ^cBinding energy $\Delta_b^{(n)} = \Delta_1^{(n)}/n = E(\text{Cl}^-) + E(\text{Na}^+) - E((\text{NaCl})_n)/n$. ^dMulliken charges Q_0 for different fold coordinated Cl atoms. ^eAverage Mulliken charges Q for all inner Cl atoms.

Table 6 B3LYP calculations for $(\text{NaCl})_n$ ($n = 4, 6, 8, 9$) clusters with 6-311G* basis sets

Cluster	$E/n / E_h$	$\Delta_1^{(n)}/\text{eV}^a$	$\Delta_d^{(n)}/\text{eV}^b$	$\Delta_b^{(n)}/\text{eV}^c$	Q_0^d	Q^e
4a	-622.653884	28.92	5.83	7.23	3c: -0.704	-0.704
6a	-622.658441	44.13	9.50	7.35	3c: -0.715	-0.732
					4c: -0.767	
8a	-622.660881	59.37	13.19	7.42	3c: -0.715	-0.751
					4c: -0.788	
9a	-622.662190	67.11	15.16	7.46	3c: -0.730	-0.766
					4c: -0.783	
					5c: -0.847	

^aCluster dissociation energy to ions $\Delta_1^{(n)} = nE(\text{Cl}^-) + nE(\text{Na}^+) - E((\text{NaCl})_n)$. ^bCluster dissociation energy to NaCl $\Delta_d^{(n)} = nE(\text{NaCl}) - E((\text{NaCl})_n)$. ^cBinding energy $\Delta_b^{(n)} = \Delta_1^{(n)}/n = E(\text{Cl}^-) + E(\text{Na}^+) - E((\text{NaCl})_n)/n$. ^dMulliken charges Q_0 for different fold coordinated Cl atoms. ^eAverage Mulliken charges Q for all inner Cl atoms.

fragments of the solid-state f.c.c. lattice are favored. Clusters with unrealistically low coordinated atoms are of reduced stability and would not be good models to represent the solid.

(ii) The topologic parameters N_d and β can be good measurements to judge the stability of clusters. For any given size, the cluster with the smallest N_d is the most stable. On the other hand, with the increase of the cluster size, the corresponding β decreases and the cluster is more stable with lower NaCl-unit energy and smoothly approaches the solid.

(iii) For the set of clusters with the smallest N_d in each given size, the NaCl-unit energy, binding energy, as well as bond distance, show a convergence from the cluster to the bulk solid. The effective charges in Cl atoms are more site dependent than size dependent. That is, the Cl atom with higher coordination number accommodates more charge, while for any given degree of coordination of a Cl atom the magnitudes of the Mulliken charges are always around a constant. In this way, with the increasing of cluster size n , the number of the high fold coordinated atoms increases and the average charge of the in-cluster atoms becomes larger.

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