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## Evolving few-ion clusters of Na and Cl

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The ground state configuration of a macroscopic quantity of Na and Cl ions is the well-known crystalline, face-centered cubic structure (table salt). However, when the number of ions is reduced to a handful, geometrically quite different and interesting ground state structures occur. Such configurations are realized in the early stages of crystal growth and are important in a growing number of physical applications. This article describes the application of a genetic algorithm to the difficult problem of the determination of the lowest-energy geometrical configurations of few-ion ( $\leq 12$ ) clusters of Na and Cl. The binding energy and the frequencies of vibration determined for these structures are compared to experimental data and to published results of other calculations. The advantages and limitations of the genetic algorithm as a tool for cluster physics are discussed.

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### I. INTRODUCTION

Sodium chloride, table salt, is an ionic crystal with a simple interleaved face-centered cubic structure of the Na and Cl ions.<sup>1</sup> This fact has been established through electron diffraction experiments which give an interion (Na–Cl) nearest-neighbor distance of  $r_0 = 2.82 \text{ \AA}$  at normal temperature and pressure. Knowledge of the structure and density of the NaCl crystal gives a second, independent measure of this distance.<sup>2</sup> A binding energy of  $-7.933 \text{ eV}$  per ion pair, with respect to charged ions at infinite separation, has been determined from experiments giving the “heat of sublimation,” that which must be given to the substance in order for it to sublime into atoms. The energy per ion pair, with respect to neutral atoms at infinite separation,  $-6.803 \text{ eV}$ , is obtained after including an electron ionization energy of Na ( $E_I = +5.14 \text{ eV}$ ) and an electron affinity energy of Cl ( $E_A$

$= -4.01 \text{ eV}$ ) (Ref. 3) which represent the energy requirements needed to form a pair of charged ions from originally neutral atoms.<sup>4</sup>

The interaction potential between two neighboring ions in the crystal consists principally of a simple point charge Coulomb attraction or repulsion (depending on whether the ion species is different or the same) and a strong repulsion at short distance due to the Pauli exclusion of the antisymmetric electron wave functions. There are also induced dipole interaction terms of the order of a few percent arising from the distortion of the electron clouds for ions in close proximity. There are other, lesser, components to the interaction energy due to the zero point quantum motion of the ions and a small amount of energy arising from a van der Waals force. These latter two contributions are small and of opposite sign and therefore normally neglected.

The binding energy of a macroscopic ionic crystal appears in solid state textbooks in the form<sup>5</sup>

$$E_B = -N \left[ \frac{\alpha e^2}{4\pi\epsilon_0 r_0} - A \exp(-r_0/\rho) \right] \quad (1)$$

or sometimes as

$$E_B = -N \left[ \frac{\alpha e^2}{4\pi\epsilon_0 r_0} - \frac{A'}{r_0^n} \right]. \quad (2)$$

The first term represents the Coulomb energy, where  $N$  is the number of ion pairs,  $r_0$  is the nearest-neighbor equilibrium distance,  $e$  is the fundamental unit of charge, and  $\epsilon_0$  is the permittivity of free space. The second term in Eq. (1) or (2) represents the repulsive Pauli energy. The constant  $\rho$  is given the value 0.317 Å for NaCl (Ref. 6) and  $n$  usually takes the value of 9.1 (Ref. 7) for this salt. From quantum mechanical considerations, the electron wave functions decrease exponentially with distance, and the more realistic form of the repulsion is that of the exponential Born–Mayer term, Eq. (1).

The constant  $\alpha$  is known as the Madelung coefficient<sup>8</sup> and represents the normalized sum of the strengths of the Coulomb interactions for all interacting ion pairs ( $i, j$ ) separated at distances  $r_{ij}$ . Thus,

$$\alpha = -\frac{1}{2} \sum_{j \neq i} \left( \frac{q_i}{q_+} \right) \left( \frac{q_j}{q_-} \right) \left( \frac{r_0}{r_{ij}} \right), \quad (3)$$

where  $q_i$  and  $q_j$  are the ionic charges of ions  $i$  and  $j$  and  $q_+$  is the ionic charge of Na (+1) and  $q_-$  that of Cl (−1). The factor of  $\frac{1}{2}$  accounts for the double counting of the interaction pairs. This sum converges for the macroscopic crystal even though the range of the Coulomb force is infinite, because of the compensating effect, becoming more complete with distance, of the alternating positive and negative charges of the crystalline structure. The result for the infinite NaCl crystal is  $\alpha = 1.748$ .<sup>3,8</sup> Likewise, the constants  $A$  or  $A'$  of Eq. (1) or (2) represent the normalized sum of the strengths of the Pauli repulsion for all interacting ion pairs in the crystal. This term converges even faster than the Coulomb term due to the rapid decrease in repulsion with ion separation. The constant  $A$  or  $A'$  is determined such that the potential gives a minimum at the experimental crystal equilibrium distance of 2.82 Å.

The convergence of both the attractive and repulsive terms of the potential,  $\alpha$  and  $A$  or  $A'$ , gives the result that the total interaction energy, Eq. (1) or (2), is proportional to the number of ion pairs,  $N$ , and not to the number of pair interactions,  $\sim N^2$ . In other words, beyond a certain crystal size at which convergence of  $\alpha$  and  $A$  or  $A'$  have occurred, the lowest energy configuration is unique. For NaCl it is found to be, at normal temperature and pressure, the interleaved face-centered cubic structure.

Below the convergence size, however, this is not true and the lowest energy structure depends on the number of pair interactions and the details of the two-body potential. We believe that this interesting fact is not adequately addressed in undergraduate treatments of the solid state. Rectification of this omission is particularly important given the recent growth in the number and variety of physical applications of atomic clusters. These applications range from elucidating crystal growth patterns,<sup>9,10</sup> to photography and catalysis where cluster size and structure are important,<sup>11</sup> to observa-

tional astronomy where knowledge of the absorption and emission bands of interstellar cluster “dust” is required for a correct interpretation of the data.<sup>12</sup> More recently, cluster physics has been instrumental in the development of the new fields of nano-electronics, where elements derive their properties from the quantum nature of the cluster,<sup>13</sup> and novel materials, where clusters instead of atoms constitute the building blocks.<sup>14</sup>

In the following section we briefly discuss the most popular theoretical approaches to determining the ground state properties of clusters. In Sec. III we define a simple two-body ion–ion potential. With a fitness function defined in terms of this potential, in Sec. IV we describe the application of a genetic algorithm to the determination of lowest energy configurations of different sized few-ion clusters of Na and Cl. In Sec. V some properties of our predicted ground states and their low-energy isomers are compared with both experimental data and published results obtained through other calculations. The advantages and limitations of the genetic algorithm approach to cluster configuration are summarized in the conclusions.

## II. CONFIGURING CLUSTERS

Theoretical determinations of cluster properties can be divided into two groups; *ab initio* and semi-empirical. *Ab initio* calculations solve the Schrodinger equation with varying degrees of approximation of the Hamiltonian for the electron–electron, electron–nucleus, and nucleus–nucleus interactions. The only empirical data going into an *ab initio* calculation are the values of the fundamental constants. Complexities arising from the many-body nature of clusters render this approach very computationally expensive, except for optimization of relatively small clusters. Also, at some cluster size, the degree of approximation of the many-body Hamiltonian cancels the benefits of the quantum calculation. However, if quantum information, such as bond breaking and accompanying electronic rearrangement or spin densities, is required, there is no substitute for the *ab initio* calculation.<sup>15</sup>

Semi-empirical approaches normally assume a two-body, central potential whose parameters are determined from experimental observables of the molecule, macroscopic crystal, or from limited cluster data. The potential depends on the distance between the ions but may also depend on induced electric dipole moments. The positions and induced dipole moments of the ions are then optimized through one of a number of sophisticated techniques with the goal of obtaining the lowest energy configuration. Fitting potential parameters to experimental data can include effects which often go beyond the scope of approximate *ab initio* calculations, and, in any case, the results of the semi-empirical approach can be used as configurational input to a full quantum calculation.

The dimensionality of the hyperspace for the search of the most stable configuration increases linearly with the number of ions in the cluster, but the complexity of the potential energy surface increases much faster than linearly with the number of ions.<sup>16</sup> Given this complexity and limited computing power, past semi-empirical investigations have been obliged to employ “intuitive” approaches which either constrain the geometry of initial configurations to “realistic” ones (particular lattice structures or symmetries) and thus to a manageable number of local optimizations,<sup>11</sup> or which constrain the search to particular sequences based on the optimization of smaller configurations. As an example of the latter,

Hoare and Pal<sup>9</sup> developed a procedure to “grow” aggregates of atoms in the computer by adding a new atom to the most “compact” surface position of an already optimized cluster and continuing the optimization with the three additional position variables of the new atom. With this procedure they found low-energy candidates for the global minimum structures of clusters of up to 55 atoms bound through a Lennard–Jones potential. Based on the icosahedral substructure of many of the ground state configurations found by Hoare and Pal, Northby<sup>17</sup> implemented a refined lattice search procedure and found new, lower energy candidates for various of the clusters below 55 atoms in size and extended the search up to cluster sizes of 147 atoms.

Such judicious selection of the symmetry dramatically reduces the dimensionality of the search space and thus the overall computational effort. However, it has become apparent that the ground state geometry can be quite different for clusters which differ in size by only one atom. Adding an atom to the most compact surface position of the configuration representing the global energy minimum of a given cluster often produces a new cluster which is separated by a large potential barrier from its true global minimum and which requires extensive collective movements of the atoms for the transformation. In other words, constrained search procedures frequently become trapped in the nearest local minimum, especially when the size of the cluster becomes large and many low-energy isomers exist with an energy close to that of the true ground state. This was recently appreciated for the Lennard–Jones cluster where still lower energy ground states than those predicted by Hoare and Pal or Northby were discovered.<sup>18</sup> For the NaCl cluster, we will demonstrate that the minimum energy structure changes abruptly from an extended two-dimensional structure to a compact three-dimensional one in going from three to four ion pairs, and, in fact, the ground state symmetries of many clusters, up to at least six ion pairs in size, are unique.

Nonconstrained stochastic techniques such as random searches and simulated annealing<sup>19,20</sup> have been applied to the cluster configuration problem.<sup>21</sup> Random searches are not efficient for problems with a complex fitness surface<sup>22,23</sup> and have generally been replaced by more sophisticated methods. Simulated annealing starts with a particular cluster configuration at a given temperature. Random displacements of individual atoms are induced with a magnitude proportional to the temperature. If a random displacement of an atom brings the cluster to a lower energy, it is accepted and the search proceeds from this new configuration. Gradually the temperature is lowered and the search becomes more and more local. This technique is an analogy of the annealing process in nature, by which, for example, liquids freeze into their lowest energy, crystal state.

A particular problem with simulated annealing is that of selecting an adequate cooling schedule since the optimal is known to be very problem specific. The ensemble approach to simulated annealing<sup>24</sup> addresses this problem by sending an ensemble of random walkers to make parallel searches of the entire configuration space simultaneously. Information on the best energy found by each walker after a given time interval provides statistics for determining the cooling schedule, and also for mapping the distribution of local minima in the complex potential energy surface. Such information is useful for studying the thermodynamic behavior of the cluster.<sup>25</sup>

Simulated annealing is often combined with molecular

dynamics<sup>21</sup> where the atomic displacements are directed by calculating the total force acting on an individual atom due to the rest of the atoms in the cluster. Applying Newton’s laws leads to a powerful dynamical method of finding low-energy configurations while also yielding thermodynamic properties of the cluster. This popular method has been applied to the configuration of both small<sup>10</sup> and large<sup>26</sup> clusters. The disadvantages are the amount of computer time required for calculating the dynamics and the problem of entrapment in local minima at low temperature which arises when a cluster has a large number of almost degenerate isomers of the ground state.

A number of so-called “intelligent” global optimization techniques have been developed in recent years. These techniques learn about the search space in which they are operating and the direction for continuing the search is determined on the basis of this accumulated historical knowledge. These techniques include the tabu search<sup>22,27</sup> and the genetic algorithm.<sup>28</sup> The tabu search borrows from the concepts of artificial intelligence and learning. It builds a table of moves and assigns desirability in a flexible memory that is continually updated. The moves may be completely forbidden or assigned a selection probability determined by the success rate of recent application. Tabu searches have outperformed simulated annealing procedures at optimization of some standard test functions.<sup>22</sup>

The genetic algorithm is an analog of nature’s biological problem solving technique. This algorithm assigns a “genetic code” to a particular cluster configuration. A population of randomly generated configurations is created as a first generation. The populations of subsequent generations are “reproduced” from previous generations through application of the genetic operators of mutation and cross over to the genetic codes of selected best fit individuals (lowest energy configurations). In this way, cluster configurations are “evolved” through generations to their lowest energy geometries. The global nature of the genetic algorithm is due to its ability to escape local minima through application of the genetic operators. It is intelligent because information regarding promising areas of the search space is accumulated in the genetic codes of the individuals and this information is exchanged among the population through the crossover mechanism.

First proposed by Holland in the 1960s in relation to work on cellular automata,<sup>29</sup> the genetic algorithm has now been successfully applied to numerous difficult problems.<sup>28,30–35</sup> Judson *et al.*<sup>23</sup> first applied the genetic algorithm to the molecular conformation problem of atoms confined to two dimensions and interacting through a Lennard–Jones potential. For resolving this problem, the genetic algorithm, combined with a local conjugate gradient minimization, was considerably more efficient than either the random search or the simulated annealing approaches. Recently, the application of the genetic algorithm to the optimization of Lennard–Jones clusters in three dimensions yielded new, lower energy predictions for the ground states of various clusters.<sup>18</sup> For a good review of the genetic algorithm published in this journal see Sutton and Boyden.<sup>28</sup>

In this article we will use the genetic algorithm to determine, in the semi-empirical approximation, the lowest energy geometries of small alkali halide clusters and obtain their binding energies and vibrational frequencies. First we define a two-body, pair-wise additive, ion–ion potential.

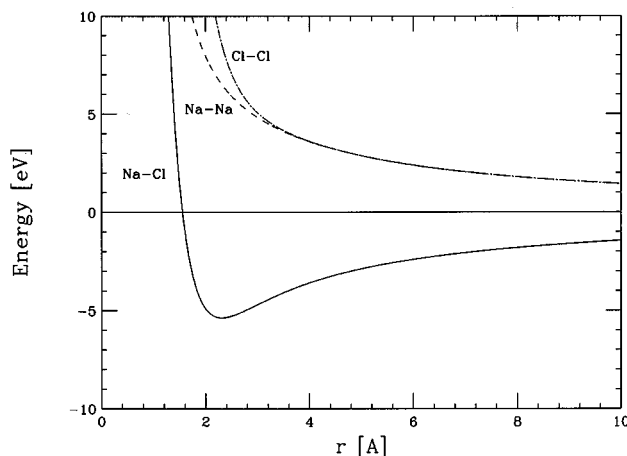


Fig. 1. The two-body ion-ion potentials.

### III. THE ION-ION POTENTIAL

We assume that the form of the binding is mainly ionic for few-ion clusters, as it is for the macroscopic crystal, and that the ionic charge states are  $+1$  and  $-1$  for Na and Cl, respectively. The large difference between the binding energy of the  $(\text{NaCl})_1$  molecule ( $\approx -4.22$  eV,<sup>7</sup> relative to neutral atoms at infinite separation) and the difference of the ionization energy of Na and the electron affinity energy of Cl ( $\approx +1.13$  eV) suggests that this is a valid assumption.

The ions  $\text{Na}^+$  and  $\text{Cl}^-$  are both noble, with closed electron shells, and thus are spherically symmetric so the Coulomb potential for ions at large separation has the simple form of a two-point charge interaction. At small separation, the electron charge distributions begin to overlap, become distorted, and dipole moments are induced. Here, however, we take the rigid sphere approximation in which there are no induced moments. Such an approximation is valid because closed electron shells act almost like rigid spheres.<sup>2</sup> The two-body potential then consists of the sum of the attractive or repulsive point charge Coulomb energy and the repulsive Pauli energy. We take the Born-Mayer form for the repulsive interaction, Eq. (1). Because the radii of the electron clouds are different for the alkali and halide ions, the coefficient of the repulsion  $A$  depends on whether the interaction is between Na-Na, Cl-Cl, or Na-Cl ions. Thus, the ion-ion potential is

$$U_{ij} = \mp \frac{e^2}{4\pi\epsilon_0 r_{ij}} + A_{ij} \exp(-r_{ij}/\rho), \quad (4)$$

where the parameters  $A$  and  $\rho$  were obtained from an analysis of crystal data by Tosi and Fumi (compiled in Ref. 6). They are  $A_{ij} = 423.80$  eV if  $i$  and  $j$  are both Na ions, 3485.23 if they are both Cl ions, and 1254.53 if one of the ions is Na and the other Cl, and  $\rho = 0.317$  Å. Equation (4) is plotted for all three interactions in Fig. 1.

The validity of Eq. (4) may be checked by comparing the predicted equilibrium distance and binding energy for the monomer  $(\text{NaCl})_1$  with that obtained from experimental data. To obtain the equilibrium distance from the potential, we differentiate Eq. (4) with respect to ion separation and set the result equal to zero. The solution of the resultant equation is  $r_{\text{eq}} = 2.312$  Å, similar to the empirical value of 2.36 Å obtained from the rotational spectrum of NaCl vapor.<sup>7</sup> Using

the predicted value of  $r_{\text{eq}}$  in Eq. (4) the predicted molecular binding energy, with respect to neutral atoms at infinite separation, is

$$E_{\text{mol}} = U_{\text{eq}} + E_I - E_A = -4.237 \text{ eV},$$

in close agreement with the empirical value of  $-4.22$  eV from thermochemical data.<sup>7</sup> Differences in the predicted and experimental equilibrium distance and binding energy can be attributed, for the most part, to neglect of the small induced dipole moments. Thus, Eq. (4), derived from the equilibrium characteristics of the NaCl crystal, predicts the equilibrium characteristics of the monomer and we should be safe in assuming that it is also valid for intermediate clusters.

### IV. THE GENETIC SEARCH

In the semi-empirical approximation with a central two-body potential, the search hyperspace for the lowest energy stable configuration of  $\text{Na}_n\text{Cl}_m$  is defined by the three position coordinates of each ion and the ion type (Na or Cl). The space thus has a dimensionality of  $4\mathcal{N}-6$  where  $\mathcal{N}$  is the number of ions and the  $-6$  results from removing the degrees of freedom associated with the translational and rotational invariance of the cluster. The invariance is most easily accounted for by choosing a Cartesian coordinate system with the  $x$  axis defined by a line joining atoms 1 and 2 and the  $y$  axis chosen to lie in the plane defined by atoms 1, 2, and 3, obtained in practice by fixing  $x_1 = y_1 = z_1 = y_2 = z_2 = z_3 = 0$ .<sup>9</sup>

Determining the ground state characteristics of the NaCl monomer from the two-body potential, Eq. (4), required only a simple differentiation. As we increase the size of the cluster, the calculation quickly becomes unwieldy (with possible configurations in two or three dimensions) and we find not one, but many local minima in the potential energy surface. Finding the lowest energy configurations of many-ion clusters therefore requires a global and efficient search method. In this work we employ the genetic algorithm. Applied to cluster configuration, the genetic algorithm proceeds as follows:

- (1) generate a random initial population of genetic codes defining distinct cluster configurations;
- (2) evaluate the fitness (binding energy) of each configuration;
- (3) generate a new population (second generation) of configurations through application of the genetic operators of crossover and mutation to the genetic codes of the best-fit configurations;
- (4) evaluate the fitness of the new generation of configurations;
- (5) repeat steps 3 and 4 for a number of generations until an adequate low-energy configuration is found.

Choosing a binary representation for each of the search variables (because of the computational facility to manipulate bit strings) genetic codes are created of the form

$$\begin{array}{cccccccccccccccccccc} I_1 & x_1 & y_1 & z_1 & I_2 & x_2 & y_2 & z_2 & \dots & I_N & x_N & y_N & z_N \\ \hline 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & \dots & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{array}$$

where the one bit representing the ion type implies a Na ion if  $I$  is equal to 1 or a Cl if it equals 0. For display purposes, each of the coordinate variables is represented here by only 3

bits and we have not removed the 6 rotational and translational degrees of freedom. In our implementation, each coordinate variable occupies 7 bits, implying  $(22 \times \mathcal{N}) - (6 \times 7)$  bits per genetic code. The number of bits per coordinate variable can be varied and determines the “coarseness” of the genetic search.

For the first generation, 50 such trial codes were created at random from the search space;

$$I_i = 0, 1 \quad \text{and} \quad -5.0 \text{\AA} < x_i, y_i, z_i < 5.0 \text{\AA},$$

which is sufficiently large to allow for all conceivable cluster configurations up to sizes of about six ion pairs. The Darwinian fitness of the code was related to the value of the cluster binding energy,  $E_B$  (the lower the energy, the more fit), where

$$E_B = \frac{1}{2} \sum_{j \neq i} U_{ij} \quad (5)$$

with  $U_{ij}$  as given by Eq. (4) and the  $r_{ij}$  determined from the ion coordinates  $x_i, y_i, z_i$  and  $x_j, y_j, z_j$ .

Of the 50 initial configurations in the first generation, the fittest 25 were selected for the “gene pool” for reproduction, the other half were discarded. The mating procedure started with a random selection of 25 two-parent pairs from the gene pool. Each pair produced two offspring codes according to the following prescription which was found to be efficient at converging on fit configurations while maintaining diversity among the population at large. Each parent pair was thus given

- (1) a 10% probability of faithful reproduction in which the offspring codes are identical to their parents,
- (2) a 3% probability of point-mutated reproduction in which one bit chosen at random of each parent code was flipped,
- (3) an 87% probability of crossover reproduction<sup>28</sup> in which the two parent codes were separated at a boundary of two genes (the variables) chosen at random and respective portions swapped to produce new offspring. This procedure is analogous to the biological process of crossing over of the genes which occurs frequently between two homologous chromosomes during meiosis to form the gametes.

In addition to the above reproduction prescription, we took the so-called “elitist” approach<sup>34</sup> by ensuring that the very best individual always reproduced an exact copy of itself for the gene pool of the following generation. With the above procedure, reproduction is constrained to keep the total population constant from generation to generation, which is a practical necessity of the algorithm.

We repeat this procedure creating a third generation by reproduction of the best fit 50% of the second generation and so on for a number of generations until little improvement in the fitness is observed from one generation to the next. For the particular cases of clusters of three and five ion pairs, the average binding energy of the fittest 50% of the configurations of each generation, and the binding energy of the best configuration of the generation, is plotted as a function of the generation number in Fig. 2. For the early generations, the increase in average fitness (decrease in binding energy) is great. The rate of average fitness improvement of the population decreases after generation number 40. This is a consequence of the fact that approaching the optimal solution re-

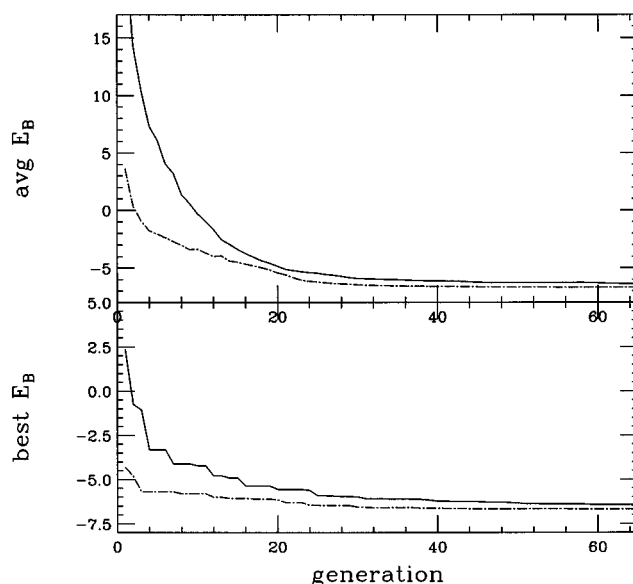


Fig. 2. The average binding energy of the 50% best fit configurations, and that of the best configuration, as a function of generation number for a three ion pair NaCl cluster (dashed lines) and for a five ion pair cluster (solid lines).

quires a reduction in the search space which would imply a loss in diversity of the population. Diversity is required at the beginning of the search to prevent trapping at a local minimum and to obtain as many distinct solutions (final configurations) as possible. However, since our definition of fitness is fixed, we would like results as near as possible to exact solutions. We therefore applied a more efficient conjugate

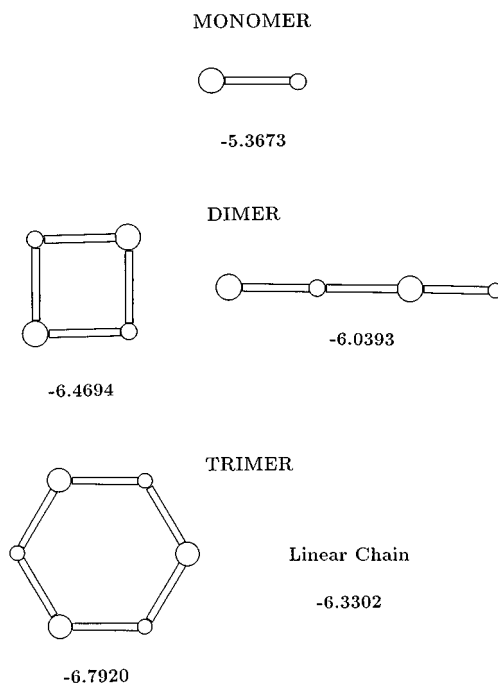


Fig. 3. The lowest energy configurations found for cluster sizes from one to three ion pairs along with their respective binding energies (eV/ion pair). The small circles are the sodium ions and the large ones are the chlorine ions.

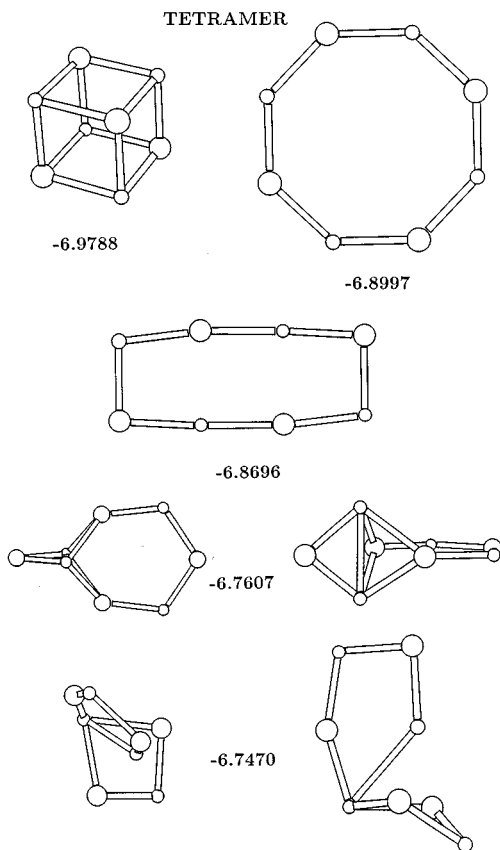


Fig. 4. The lowest energy configurations found for the cluster size of four ion pairs along with their respective binding energies (eV/ion pair).

gradient local minimization<sup>20</sup> (to a precision of  $\Delta E_B/E_B < 10^{-7}$ ) to the 10 best distinct configurations after 50 generations of genetic evolution.

## V. RESULTS

The five lowest energy configurations found for cluster sizes of one to six ion pairs are shown, along with their corresponding binding energies (eV per ion pair), in Figs. 3–6. Two mutually perpendicular views are given for most of the three-dimensional clusters to help in the interpretation of the structure. The figures are not schematic but actual visualizations of structures found. For clarity, the ion sizes are not drawn to scale, and ions are connected by rods if the ratio of the distance between the ion centers to the sum of their radii is less than or equal to 1.12.

We note first that the number of halide ions is equal to the number of alkali ions ( $m=n$ ) in all of the low-energy configurations found. The two-dimensional ring configuration is seen to be the most strongly bound for clusters up to three ion pairs. Beyond this number of pairs, the ground-state structures are three-dimensional but the two-dimensional isomers are still competitive. Note that the three ion pair double chain doesn't appear in Fig. 3 as it is not stable. At four ion pairs, the two-dimensional ring is more tightly bound than the two-dimensional double chain, but at five and six ion pairs the reverse is true. It is interesting to note that many ground-state structures have a unique symmetry and that most of these structures and the isomers are not based on the face centered cubic structure of macroscopic NaCl.

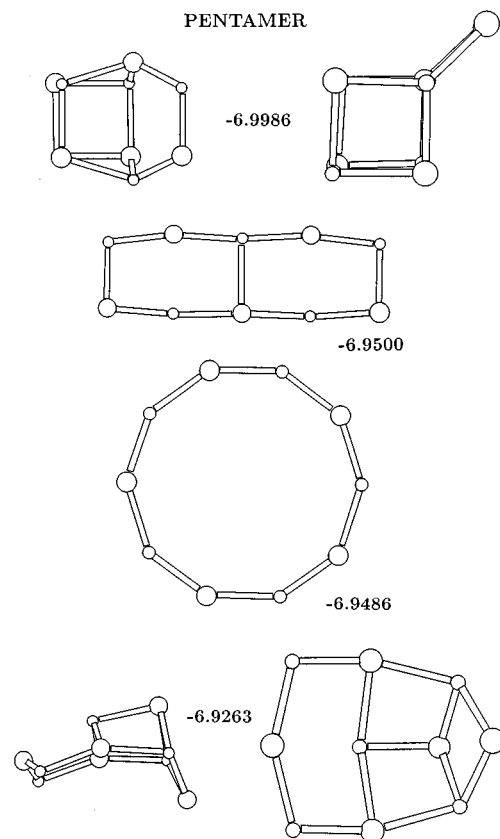


Fig. 5. The lowest energy configurations found for the cluster size of five ion pairs along with their respective binding energies (eV/ion pair).

At finite temperatures, vibrational excitation of the cluster is possible. The vibrational modes of oscillation of a particular configuration, in the harmonic oscillator approximation, can be predicted from the second derivatives of the binding energy, Eq. (5), with respect to ion displacements at the equilibrium configuration.<sup>7</sup> For the multi-dimensional potential surface, a  $3N \times 3N$  dynamical matrix is constructed of the following form:

$$\begin{pmatrix} \frac{\partial^2 E_B}{\partial x_1^2} & \frac{\partial^2 E_B}{\partial x_1 \partial y_1} & \frac{\partial^2 E_B}{\partial x_1 \partial z_1} & \frac{\partial^2 E_B}{\partial x_1 \partial x_2} & \dots \\ \frac{\partial^2 E_B}{\partial y_1 \partial x_1} & \frac{\partial^2 E_B}{\partial y_1^2} & \frac{\partial^2 E_B}{\partial y_1 \partial z_1} & \frac{\partial^2 E_B}{\partial y_1 \partial x_2} & \dots \\ \frac{\partial^2 E_B}{\partial z_1 \partial x_1} & \dots & \dots & \dots & \dots \\ \vdots & & & \ddots & \end{pmatrix}. \quad (6)$$

Diagonalization of this matrix gives the eigenvalues which are the force constants  $k$ . Six of the eigenvalues will be zero, corresponding to the degrees of freedom which must be removed due to the translational and rotational invariance of the cluster. The force constants are related to the wave number  $1/\lambda$  of the vibrational modes through

$$\frac{1}{\lambda} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2}, \quad (7)$$

where  $c$  is the speed of light in vacuum and  $\mu$  is the reduced mass

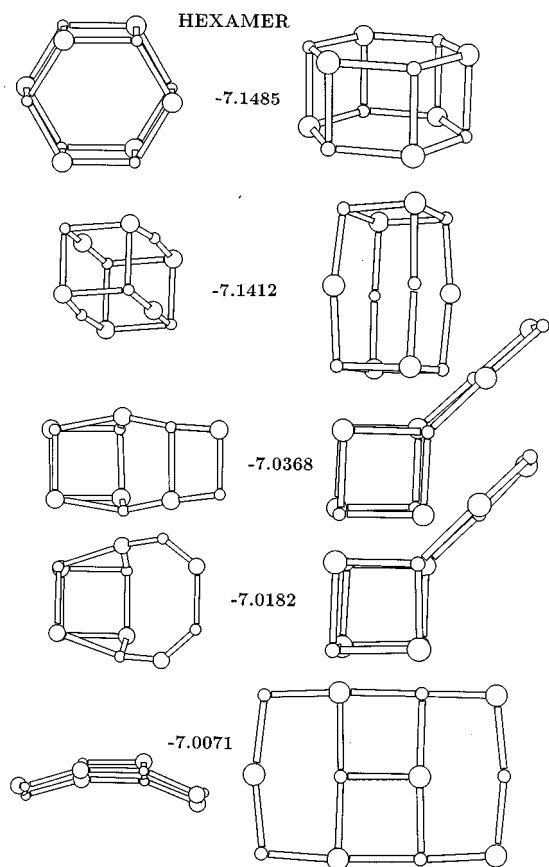


Fig. 6. The lowest energy configurations found for the cluster size of six ion pairs along with their respective binding energies (eV/ion pair).

$$\mu = \frac{M_{\text{Na}} M_{\text{Cl}}}{M_{\text{Na}} + M_{\text{Cl}}} \quad (8)$$

Local minimization of a given configuration leads to either a true minimum or a saddle point in the potential energy surface. An analysis of the eigenvalues of the dynamical matrix, however, can distinguish between these two cases. If the configuration is a true minimum, real positive wave numbers result. If the configuration is a saddle point, at least one of the wave numbers will be imaginary (corresponding to  $k$  negative). This analysis of the dynamical matrix is equivalent to checking the values of the second derivative of the binding energy at the declared minimum to determine whether the point is a true minimum, maximum, or a point of inflection (saddle point). All of the configurations presented in Figs. 3–6 gave real wave numbers and thus are true minima. Saddle points, with one small imaginary frequency, encountered during the optimization process are presented in Fig. 7. For the one mode of vibration of the monomer (NaCl)<sub>1</sub> we found  $1/\lambda = 346.41 \text{ cm}^{-1}$ , in close agreement with the experimental value of  $336 \text{ cm}^{-1}$  (Ref. 6). The vibrational spectra for the most-bound configuration of cluster sizes of two to six ion pairs are presented in Fig. 8.

The alkali halide cluster has been studied previously through a number of distinct techniques. Since almost all works have used a slightly different potential, a quantitative comparison of the energies of the configurations is not meaningful. Instead, we compare the geometrical configurations and their sequence in energy.

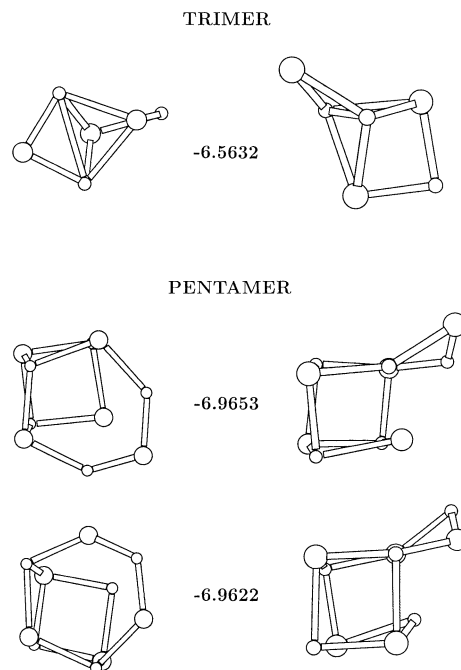


Fig. 7. Saddle point configurations encountered during the optimization for the cluster sizes of three and five ion pairs along with their respective binding energies (eV/ion pair).

Welch *et al.*<sup>36</sup> studied the NaCl monomer, dimer, and trimer, using a potential identical to ours but which also included the interaction of induced electric dipole moments. In this case, comparison of energies provides a measure of the importance of including these moments in the interaction potential. The geometries of the ground state configurations found by Welch *et al.* are equivalent to those found in this work. The ratios of the binding energies of the ground state (this work/Welch *et al.*) are 0.934, 0.960, and 0.980 for the monomer, dimer, and trimer, respectively. Similarly, the ratios of the equilibrium distances (between neighboring Na and Cl ions) are 0.980, 0.986, and 0.991 for the monomer, dimer, and trimer, respectively. Welch's results are in good

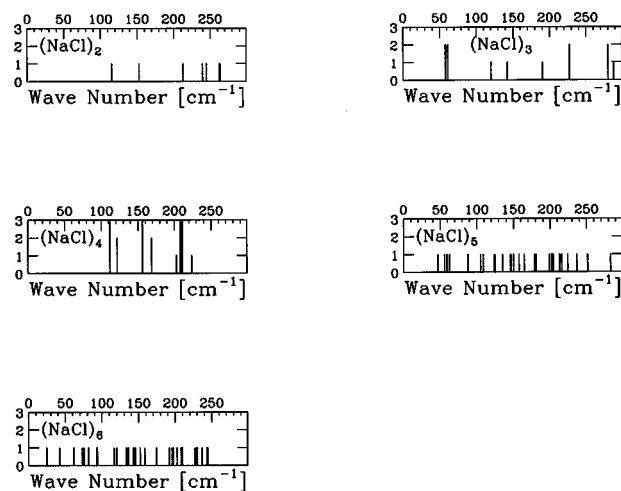


Fig. 8. The vibrational spectra for the most stable configuration of each cluster size.



agreement with the available experimental data for the monomer, giving 5.75 eV [compared to the experimental values of 5.35 eV,<sup>7</sup> and 5.81 eV (Ref. 37)] for the binding energy relative to ions at infinite separation, and 2.36 Å [compared to the experimental values of 2.36 Å,<sup>7</sup> 2.36 Å,<sup>37</sup> and 2.388 Å (Ref. 38)] for the equilibrium distance. It is interesting to note that whereas we found the NaCl linear dimer to be a stable configuration, Welch *et al.* found it to be unstable with induced electric dipole moments included. From this comparison we conclude that the electric dipole interaction is of only slight importance to the energy and geometrical configuration of the ground state for small clusters and plays an increasingly reduced role for larger clusters (further verified through our own optimizations of much larger NaCl clusters<sup>39</sup>). However, inclusion of dipole moments can influence the stability of certain cluster configurations which lie in shallow potential wells.

Martin<sup>11</sup> has published an extensive study of the NaCl cluster up to 32 ions in size, using a potential not including the dipole interactions, in which a large number of “intuitive” initial configurations were minimized locally. Our geometrical configurations for the one to four ion pair clusters and their sequence in energy are identical to those obtained by Martin although our energies are slightly lower since Martin assumed equal repulsive potentials for the Na–Na, Cl–Cl, and Na–Cl interactions. For the five and six ion pair systems, however, significant differences were found. First, unlike in Martin’s depiction of the lowest energy pentamer (the capped-cube configuration), we found that the cap on the cube opens up to form a ring (see Fig. 5). Second, we found the pentamer double-chain structure to be more tightly bound than the ring structure. The fourth structure in energy also appears to be distinct from the one found by Martin. Our fifth structure in energy for the pentamer is equivalent to our fourth structure but with the Cl ions replaced by Na ions and vice versa (not shown in Fig. 5). The energy of this structure was determined to be  $-6.9245$  eV. For the hexamer, contrary to Martin’s results, we found the double ring to be more tightly bound than the rectangular structure. Many new minima were found with significantly lower energy than Martin’s third-in-energy, double-chain structure. Three such structures are listed in Fig. 6. The differences between our findings and those of Martin can be attributed in part to the differences in the potential used and in part to the fact that, at this size of cluster, there are many local minima and the “intuitive” or random local search procedures are not sufficiently global.

Häkkinen *et al.*<sup>40</sup> have studied the structures and energies of the ground state configurations of  $(\text{NaCl})_n$ ,  $1 \leq n \leq 4$ , using a local-spin-density functional calculation (quantum, *ab initio* calculations). The geometries of these configurations correspond to those of ours. However, they find that the double-chain trimer isomer is stable whereas our, Martin’s, and Welch’s semiempirical calculations predict it to be unstable. The binding energies per ion pair they find for the monomer, dimer, trimer, and tetramer ground states are 5.53, 6.54, 6.76, and 7.01 eV, respectively [including an “exchange-correlation gradient correction”,<sup>40</sup> and assuming an electron affinity energy of Cl of  $-4.01$  eV and an electron ionization energy of Na of  $+5.14$  eV (Ref. 2)]. These values fluctuate slightly around the results obtained with semiempirical calculations (see, for example, Figs. 3 and 4). The equilibrium distance they calculate for the monomer is 2.386

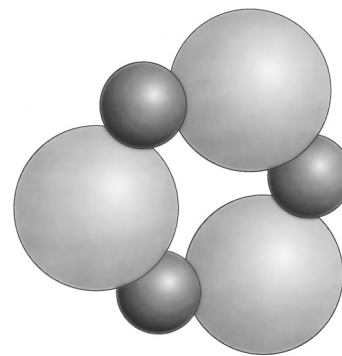


Fig. 9. True scale model of the lowest energy configuration found for a cluster size of three ion pairs. The large spheres are the Cl ions and the small ones are the Na ions.

Å, consistent with experimental data and semiempirical calculations including dipole interactions, but about 3% larger than our value.

The alkali halide systems  $(\text{KCl})_4$  and  $(\text{KCl})_5$  have been studied by Rose and Berry<sup>10</sup> through molecular dynamics using a two-body potential similar to ours. The three most tightly bound minimum energy configurations we found for  $(\text{NaCl})_4$  are in agreement with those found by Rose and Berry for  $(\text{KCl})_4$ . For  $(\text{NaCl})_5$ , our second most tightly bound configuration (the distorted capped-cube) was found to be a saddle point (see Fig. 7) and not a true minima as reported by Rose and Berry for the system  $(\text{KCl})_5$ . We attribute this to the differences in the repulsive Pauli interaction for the Na–Cl and K–Cl systems.

Figure 9 shows a true scale model of our predicted ground state geometry for the cluster size of three ion pairs.

One run of the genetic algorithm required approximately 0.21 s CPU time on a DEC Alpha Station 500 (266 MHz) and was sufficient to consistently find all the lowest energy configurations reported for clusters up to three ion pairs in size. For four to six ion pairs, three runs of approximately 0.46 s CPU time each were sufficient to find the lowest energy closed structure configuration if the search space was confined to a box of 5 Å dimension, and approximately ten runs for the open configurations in a box of 10 Å dimension.

## VI. DISCUSSION AND CONCLUSIONS

The low-energy configurations presented in this work are those which would be the most probable at  $T=0$  K. At finite temperatures the vibrational modes of the configurations are important and we should minimize the free energy rather than the potential. This implies that some configurations which are more energetically probable at low temperature are not necessarily the most probable at higher temperature. The lower the vibrational frequency of the intrinsic modes of the configuration, the more likely it is to exist at higher temperature. However, there is no single configuration which is predicted to occur exclusively; all of the low-energy configurations found here will occur at any temperature with varying probability dependent on their natural frequencies.<sup>11</sup>

Induced dipole moments are generated for ions in close proximity but we have neglected this contribution to our interaction potential. In the previous section we have seen that this results in slightly smaller values of both the binding energy and the interion equilibrium distances for small clus-

ters. However, the dipole interaction is important to the question of cluster stability. The charge–dipole, dipole–dipole, and self-dipole energy must be taken into account in a more exact calculation. It is straightforward to extend the optimization to the electric dipole moments by including in the genetic code another three variables per ion, defining the vector moment. The results of this extension are not too different and will shortly be published along with results for larger sized NaCl clusters and other alkali halide salts.<sup>39</sup>

Genetic algorithms are endowed with a number of characteristics which suggest their potential utility as an effective tool for configuring clusters. First, they are efficient because they optimize the time spent between looking for solutions in new regions of the search space and exploiting the good regions already found. In fact, it has been shown that Darwin fitness-proportionate reproduction assigns a mathematically nearly optimal allocation of trials to the different regions of the search space.<sup>29</sup> Their efficiency is further enhanced by the fact that they are implicitly parallel: In evaluating the fitness of a solution, they are also evaluating the fitness of partial solutions, called “schemata,” consisting of continuous or noncontinuous subsets of the genetic code.<sup>33</sup> Information obtained through the fitness evaluation is preserved in the genetic codes and exchanged among the population of solutions through the processes of selection and crossover. Second, genetic searches are complete and global in the sense that no regions of the search space are inaccessible and mutation and crossover reduce the possibility of trapping at local minima, which inevitably happens with local searches for the global minimum on the complex cluster potential energy surface.

Although the genetic algorithm is not a deterministic approach, such as, for example, molecular dynamics, neither is it strictly stochastic. The individuals of a given generation are determined to a large extent by the successful individuals of the previous generation. By maintaining diversity in the population through including not only the very fittest individuals in the gene pool, and by employing the crossover operation, the search is directed in an optimal manner to check the fitness of combinations of fit schema. The advantages of this approach over deterministic dynamical approaches are: the savings in the computational time required to calculate the dynamics; the insensitivity of the search efficiency, and the final result, to the starting configuration; and the ability to avoid entrapment in local minima. The principal advantage of this approach over stochastic approaches is a significant improvement in the efficiency obtained through its ability to acquire and use historical knowledge of the fitness surface to direct the search to promising regions.

Genetic algorithms have been termed a “bottom up” approach in that solutions to problems can be obtained with little *a priori* assumption or knowledge of the problem domain or the solution space. All that is needed is a means of defining the fitness of a solution. For this reason “intuition” can be dispensed with, allowing for a multiplicity of untemplated cluster configurations to be found.

Finally, genetic algorithms can easily be programmed and adapt nicely to parallel computing environments.

The most important limitation of the genetic algorithm with regard to cluster physics is its inability to directly determine thermodynamic properties of the cluster such as the solid/liquid/gas transition temperature and dynamics.<sup>41</sup> However, the dynamics of a cluster are intimately related to the

structure and energetics of the ground state and its isomers.<sup>10,25</sup> Therefore, a quick and thorough survey of the configuration minima and saddle points provides substantial insight into the interpretation of molecular dynamic results. We suggest further that coupling the genetic algorithm to the more sophisticated molecular dynamic or *ab initio* calculations through the use of the evolved cluster minima as initial configurational input should provide an efficient and powerful tool for cluster physics.

Cluster physics is an important new science with many potential applications. We have presented a simple introduction to cluster physics normally not included in undergraduate solid state courses and have suggested an accessible new tool, the genetic algorithm, for the development of this science.

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