Structure of Mg$_n$ and Mg$_n^+$ clusters up to $n = 30$

S. Janecek$^{1,2}$, E. Krotscheck$^{2,3}$, M. Liebrecht$^2$, and R. Wahl$^{2,4}$

$^1$ Institut de Ciència de Materials de Barcelona (ICMAB–CSIC), Campus de Bellaterra, 08193 Barcelona, Spain
$^2$ Institute for Theoretical Physics, Johannes Kepler Universität Linz, A-4040 Linz, Austria
$^3$ Department of Physics, University at Buffalo SUNY Buffalo NY 14260
$^4$ Faculty of Physics and Center for Computational Materials Science, University of Vienna, A-1090 Vienna, Austria

Abstract. We present structure calculations of neutral and singly ionized Mg clusters of up to 30 atoms, as well as Na clusters of up to 10 atoms. The calculations have been performed using density functional theory (DFT) within the local (spin-)density approximation, ion cores are described by pseudopotentials. We have utilized a new algorithm for solving the Kohn-Sham equations that is formulated entirely in coordinate space and, thus, permits straightforward control of the spatial resolution. Our numerical method is particularly suitable for modern parallel computer architectures; we have thus been able to combine an unrestricted simulated annealing procedure with electronic structure calculations of high spatial resolution, corresponding to a plane-wave cutoff of 954eV for Mg. We report the geometric structures of the resulting ground-state configurations and a few low-lying isomers. The energetics and HOMO-LUMO gaps of the ground-state configurations are carefully examined and related to their stability properties. No evidence for a non-metal to metal transition in neutral and positively charged Mg clusters is found in the regime of ion numbers examined here.

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1 Introduction

The properties of nanometer-sized clusters of atoms are significantly different from those of the isolated chemical species as well as the bulk material, and generally exhibit a strongly non-monotonous size-dependent behavior [1]. Clusters are the ultimate nanostructures, where a fundamental understanding of their properties can be achieved one atom and one electron at a time. They thus open a unique window to study the emergence of the properties of macroscopic matter from its microscopic constituents, and have become an active field in basic research. Nanostructured materials also hold, due to low dimensionality and unique composition, the promise of technological applications reaching as far as clean and sustainable energy, reactions, and catalysis [2,3].

The transition from microscopic to macroscopic behavior is particularly obvious for clusters of atoms that are bound by covalent bonds at small atom numbers, but are metals in bulk quantities. These must, at some point, undergo a transition to metallic behavior.

The history of the examination of these clusters is long; we take a fresh view for a number of reasons: One is that we present here the first large-scale application of limerec [4], a new open source Density Functional Theory (DFT) package specifically designed for cluster calculations. The method is formulated entirely in real space. It thus avoids any basis set bias and is particularly suited for modern parallel computing environments [5,6,7]. Due to its efficiency, the method allows to find ground state configurations and low-lying isomers of fairly large clusters by unrestricted minimization of the total energy in the whole configuration space, using Langevin-Monte-Carlo and/or steepest descent annealing procedures. It thus also eliminates a possible bias due to the choice of a certain symmetry or starting configuration that is present in more restricted minimization schemes. Our second objective is to prepare for studying the influence of a quantum fluid matrix on the formation and structure of metallic clusters in the near future.

The main thrust of this paper is to present a detailed and systematic characterization of neutral and singly ion-
ized magnesium clusters of up to 30 atoms. We also discuss some sample calculations for smaller sodium clusters, mostly for the purpose of studying electron localization. All calculations have been performed in the framework of spin-density functional theory (SDFT), using the Perdew-Wang exchange-correlation functional \cite{Perdew96} and local \cite{LDA} as well as norm-conserving non-local pseudopotentials \cite{Ceperley} to treat the core electrons. In addition to the spatial structures of the ground state configurations and low-lying isomers, we also report binding energies, ionization energies and fragmentation energies as well as the HOMO-LUMO gap for all clusters. Details of the computational method are given in section 2.

We have chosen to study mostly Mg\textsubscript{n} and Mg\textsuperscript{+}\textsubscript{n} clusters for a number of reasons: The simpler analog, Na\textsubscript{n} clusters, has been studied extensively, see, for example, Ref. \cite{NaCl} for a recent review as well as references to earlier work. Although there are still some open issues \cite{NaOpen}, Na\textsubscript{n} clusters are reasonably well described by a simple jellium model, in particular energetic quantities like magic numbers are well reproduced. In Mg\textsubscript{n} clusters, electrons are more strongly localized and, hence, a jellium model is less appropriate. Comparing Mg\textsubscript{n} and Na\textsubscript{n} clusters can therefore tell us about the consequences of electron localization.

A striking feature is that Mg\textsubscript{n} clusters evolve, with increasing ion number \(n\), from molecule-like complexes bound by covalent bonds to a bulk metal where the valence electrons are delocalized. For Mg clusters in helium, this non-metal to metal (NMM) transition has been reported to occur around \(n = 20\) with different experimental techniques \cite{MgHe}. Thomas \textit{et al.} \cite{MgHe}, for example, have measured photoelectron spectra of mass-selected magnesium cluster anions, which are related to the HOMO-(HOMO-1) gap. Similar results have been reported for Cd clusters \cite{Cd}. We note, however, that the experimental evidence of NMM transitions is rather indirect. Refs. \cite{NaOpen} \cite{NaOpen} \cite{NaOpen} argue that due to the method of measurement, the observed NMM transition may even depend on the formation process. For a review and discussion, see Ref. \cite{MgReview}.

The size range where the NMM transition has been proposed is easily accessible by DFT calculations. We will contribute to the discussion here by studying the development of HOMO-LUMO gaps as a function of cluster size, and by looking at the degree of localization of the electronic density.

Another objective of our work is to prepare for the study of metallic clusters in quantum fluid matrices. Techniques to agglomerate atoms and small molecules in a quantum fluid matrix — specifically, in superfluid \(^4\text{He}\) — have opened a new and versatile way to study the structural, electronic and spectroscopic properties of nanoparticles. The helium droplets can be viewed as ultracold nanoscopic reactors, which isolate single molecules, clusters, or even single reactive encounters at very low temperatures \cite{HeDroplets}. Clusters of well-defined composition can be formed inside the droplets, and their examination in the millikelvin regime has already given important clues on magnetism and superconductivity on the nanometer scale \cite{HeDroplets}.

There is increasing evidence that the presence of a helium matrix can indeed change the geometric arrangement and other properties of the metal cluster ions. For example, cluster growth by capturing in \(^4\text{He}\) droplets can lead to different isomers, which are not found with other cluster generation techniques and which may be affected differently by the He environment. Such an effect has been observed for clusters bound by hydrogen bridges: Cyclic water hexamers were found in helium droplets, but not in vacuum \cite{WaterDroplets}. There is also evidence that the feedback of the surrounding quantum fluid on the much more strongly bound carbon nanotubes is non-negligible; Kim \textit{et al.} \cite{Kim} point out that this is basically dictated by Newton’s third law. An unambiguous interpretation of such experiments requires understanding of the influence of the \(^4\text{He}\) surrounding the cluster. Also, metallic clusters that are difficult to generate in vacuum can be formed in a fluid matrix \cite{MetalDroplets}. Liquid helium provides an ideal medium for such “nanoreactors” because it is transparent in the entire spectral range from the far IR to vacuum UV, and high spectroscopic resolution, comparable to the gas phase, can be achieved.

Our paper is organized as follows: In Sec. 2 we give a brief discussion of the computational methods used. The core of our DFT package is a diffusion algorithm for solving Schrödinger-like equations; a more extensive analysis of the method, including convergence tests, a comparison with the implicitly restarted Lanczos method and an assessment of its performance on parallel computing architectures, has been given in Ref. \cite{DFT}. A separate program package for solving the Schrödinger equation for the bound states in an arbitrary local potential is also available \cite{ODE}. Sec. 3 turns to the results of our calculations. We briefly study Na\textsubscript{n} and Na\textsuperscript{+}\textsubscript{n} clusters and determine their structure and energetics. A somewhat unexpected feature is that local pseudopotentials predict a distorted ground state configuration of Na\textsubscript{4}. We then turn to our discussion of Mg\textsubscript{n} and Mg\textsuperscript{+}\textsubscript{n} clusters. We present results for the ground state configuration, energetics, and stability of these systems and examine the appearance and origin of “magic numbers”. The concluding section 4 gives a brief summary of our findings.

2 Computational Methods

2.1 Spin-Density Functional Theory

Spin-density functional theory \cite{SDFT} maps the solution of the interacting many-electron problem onto that of a non-interacting auxiliary system, which is described by the Kohn-Sham equations,

\[ \left( \frac{\hbar^2}{2m} \nabla^2 + V_{KS} \right) \psi_j^\sigma (\mathbf{r}) = \epsilon_j^\sigma \psi_j^\sigma (\mathbf{r}), \quad (1) \]

\[ \rho(\mathbf{r}) = \sum_\sigma \sum_j n_j^\sigma |\psi_j^\sigma(\mathbf{r})|^2 \equiv \sum_\sigma \rho^\sigma (\mathbf{r}). \quad (2) \]

These are non-linear Schrödinger equations for a set of single-particle wave functions \(\psi_j^\sigma(\mathbf{r})\) in an effective poten-
tial $V_{KS}^{\sigma}[(\rho^\sigma)](r)$, where $\sigma$ denotes the spin index and $n^\sigma_j$ is the occupation number of the state $\{j, \sigma\}$. The effective potential

$$V_{KS}^{\sigma}[(\rho^\sigma)](r) = V_{\text{ext}}(r, \{R_i\}) + V_C[\rho](r) + V_{\text{xc}}[(\rho^\sigma)](r)$$

(3)

consists of the external potential $V_{\text{ext}}(r, \{R_i\})$ describing the interaction of the valence electrons with the ion cores located at the positions $\{R_i\}$, the Coulomb term

$$V_C[\rho](r) = \int \frac{\epsilon^2}{|r - r'|} \rho(r') \, d^3r',$$

(4)

which accounts for the direct electron-electron interaction, and the exchange-correlation potential $V_{\text{xc}}[(\rho^\sigma)](r)$. In this work, the local spin-density approximation [26] is used for $V_{\text{xc}}$, with the correlation functional proposed by Perdew and Wang [8].

Equations (1) and (2) are solved self-consistently for each set of ion positions $\{R_i\}$. To find the global minimum of the total energy, the energy function $E(\{R_i\})$ must be evaluated at many different points in configuration space. Thus, an indispensable prerequisite for performing an unrestricted minimization is a fast and reliable method to solve the Kohn-Sham equations.

### 2.2 Diffusion algorithm

In recent years, real-space methods for solving the Kohn-Sham equations [1, 2] have become increasingly popular [27, 28]. They are easy to implement, free from modeling uncertainties, and well suited for modern massively parallel computers. The calculations in this work have been performed using the program package limerec [4], which solves the Kohn-Sham equations on a real-space grid using an efficient diffusion algorithm: The lowest $n$ eigenstates of the one-body Schrödinger equation

$$(T + V)\psi_j(r) = E_j\psi_j(r)$$

(5)

are obtained by repeatedly applying the imaginary time evolution operator

$$\mathcal{T}(\epsilon) \equiv e^{-\epsilon(T+V)}$$

(6)

to a set of trial functions $\{\psi_j(r)\}$, which are orthogonalized after each step. Above, $T$ is the one-body kinetic energy operator, and $V$ the potential. The operator $\mathcal{T}(\epsilon)$ multiplies states corresponding to higher energies by exponentially decreasing weights. It thus gradually filters out high-energy states, making the procedure converge to the lowest $n$ eigenstates of the operator $T + V$.

The evolution operator $\mathcal{T}(\epsilon)$ can not be calculated exactly. A simple approximation is the so-called split operator form [29],

$$\mathcal{T}_2(\epsilon) \equiv e^{-\frac{i}{2}V} e^{-\epsilon T} e^{-\frac{i}{2}V} = e^{-\epsilon(T+V+\mathcal{O}(\epsilon^2))};$$

(7)

it is accurate up to second order in the timestep $\epsilon$.

Factoring $\mathcal{T}(\epsilon)$ obviously reduces the problem of calculating the exponential of the full Hamiltonian to the problem of dealing with its parts separately. For a local operator $V(r)$, the action of $e^{-\epsilon V}(r)$ on a function $\psi_j(r)$ is just a vector-vector multiplication. The operator $e^{-\epsilon T}$ is local in momentum space, its action on a given state needs one Fast Fourier Transform (FFT) pair (forward and backward) in addition to a vector-vector multiplication in Fourier space. If $\psi_j(r)$ is represented by its values at $N$ grid points, these operations scale with $\mathcal{O}(N)$ and $\mathcal{O}(N \log N)$, respectively.

The timestep-dependent error $\mathcal{O}(\epsilon^2)$ introduced by the decomposition process imposes an upper limit for the time step if a certain accuracy has to be reached. On the other hand, the whole procedure needs fewer iterations when the time step is large. To achieve faster convergence, it would be desirable to use higher order algorithms at larger time steps. Unfortunately, Sheng [30] and Suzuki [31] have shown that no factorization of the evolution operator into a product of the operators $e^{-\alpha \epsilon V}$ and $e^{-\beta \epsilon T}$ beyond second order can have all positive coefficients $\alpha, \beta$. This so-called forward time step requirement is, however, essential for the numerical stability of the algorithm. Fourth order algorithms with exclusively positive time steps have been derived by Suzuki [32, 33] and Chin [34] by introducing an additional correction to the potential of the form $[V, T, V]$. This correction term has first been used by Takahashi and Imada [35]. We have shown previously [36] that these forward fourth-order algorithms can achieve similar accuracy at more than an order of magnitude larger step sizes compared to second-order splitting (7).

### 2.3 Multi-product expansion

Recently, we have made important progress in deriving higher-order factorization schemes [7, 25] by using a linear combination of second-order propagation steps,

$$\mathcal{T}_{2n}(\epsilon) \equiv \sum_{k=1}^n c_k \mathcal{T}_2^k \left( \frac{\epsilon}{k} \right) = e^{-\epsilon(T+V+\mathcal{O}(\epsilon^2))}. $$

(8)

The coefficients $c_k$ are given in closed form for any $k$ [37]. We have recently implemented a diffusion algorithm based on such an expansion [7, 25]. One 2n-th order propagation step $\mathcal{T}_{2n}(\epsilon)$ requires $n(n+1)/2$ second-order propagation steps. This is more than outweighed by the fact that much larger timesteps can be used for the higher-order algorithms due to the smaller time-step error. For instance, we have shown in Refs. [7, 25] that the 12-th order algorithm, which requires 21 second-order propagations, yields the same accuracy as the underlying second-order scheme at a time step about a factor of 1000 larger. The advantage of high-order propagation methods is particularly compelling on parallel computer architectures: The calculation of the action of the evolution operator $\mathcal{T}(\epsilon)$ on the wave functions can be parallelized efficiently by simply distributing the wave functions $\psi_j(r)$ across different processors. As higher-order algorithms need much
fewer, but more expensive propagation steps, the relative weight of orthogonalization, which can be parallelized less efficiently, decreases. Consequently, the parallel speedup ratio is higher for higher-order algorithms [7].

### 2.4 Pseudopotentials

Chemical binding properties are almost exclusively determined by the valence electrons, a fact that is particularly true for metals like sodium and magnesium where the s-type outer electrons are well separated from a noble gas type ion core. The idea to ignore the strongly bound core electrons in calculations and to reduce the nucleus and the core electrons to a “black box”, an ion core that interacts with the valence electrons by means of an effective pseudopotential, dates back to Fermi [38].

Pseudopotentials used in modern electronic structure calculations generally fall into two categories: One type, empirical pseudopotentials, uses an analytic model potential with parameters that are fitted to experimental data. So-called *ab-initio* pseudopotentials, on the other hand, are obtained by inverting the free-atom Schrödinger equation for a given reference configuration [39], and enforce the pseudo-wave functions to coincide with the true all-electron wave functions outside a given core radius. The pseudopotentials in this group are usually non-local. The diffusion algorithm, which was presented for local potentials in Sec. 2.2 has also been implemented for non-local pseudopotentials [6]. The program package limerec supports both local as well as norm-conserving non-local pseudopotentials in the form generated by the fhi98pp pseudopotential generator. Most calculations in this work have been carried out using the local, empirical potentials of Fiolhais et al. [9]. For the purpose of testing the sensitivity of our results to the pseudopotential used, we have performed the calculations for Na clusters also with the potential proposed by Kümmel et al. [10]. In one case, the local potentials predicted a ground state structure different from what has been reported in the literature. In this case, we have checked the calculations using non-local Troullier-Martins pseudopotentials [11].

### 2.5 Structure optimization

For structure optimization, we have used a simulated annealing procedure based on Langevin [11] dynamics of the ions and a steepest descent method. The Langevin method is similar to the Metropolis algorithm [12], but additionally takes into account the influence of forces on the particles. The ions at positions \( \{ \mathbf{R}_i \} \) are moved according to

\[
\mathbf{R}^{(N+1)}_i = \mathbf{R}^{(N)}_i + \delta x_i \mathbf{g}(i) - \frac{\beta}{2} \delta x^2 \mathbf{F}^{(N)}_i,
\]

where \( \mathbf{g}(i) \) is a sequence of Gaussian random numbers, \( \delta x \) is a factor that determines the amplitude of the random walk of the atoms, \( \mathbf{F}^{(N)}_i \) is the force on the \( i \)-th atom in simulation step \( N \), and \( \beta = 1/(k_B T) \), where \( T \) is an artificial temperature. The forces on the ions can be calculated from a single DFT calculation at fixed ion positions \( \{ \mathbf{R}_i \} \) using the Hellman-Feynman theorem [43,44]. After each move, the energy difference

\[
\Delta E = E[\{ \mathbf{R}^{(N+1)}_i \}] - E[\{ \mathbf{R}^{(N)}_i \}]
\]

is calculated, where \( E[\{ \mathbf{R}^{(N)}_i \}] \) is the energy of the cluster at fixed ion positions \( \{ \mathbf{R}_i \} \) at step \( N \), as calculated by DFT. If \( \Delta E < 0 \), the move is accepted in any case, for \( \Delta E > 0 \), the move is accepted with a probability \( \exp(-\beta \Delta E) \). Compared to the Metropolis algorithm, Langevin dynamics allows for higher acceptance rates.

Langevin simulated annealing is guaranteed to converge to the global energy minimum asymptotically, i.e., in the limit of infinitely many annealing steps. For a detailed analysis of the convergence properties of the method, including the finite-time behavior, see Ref. [45]. In practical calculations, cooling the system faster or terminating the annealing process earlier leads to an increased probability of freezing it in a higher-lying, local energy minimum. One way to verify the robustness of the procedure is to repeat it from different starting configurations. To find the ground-state configurations and isomers reported in this work, we have thus proceeded as follows:

1. We have generated a number of random starting configurations of ion core positions for each cluster, only ensuring that the distances between the ion cores are large enough to avoid divergences. If only ground-state configurations are of interest, the annealing process can in principle be stopped as soon as it becomes clear that it converges towards a higher energy than a previously found configuration. To find isomers, we have nevertheless completed the full annealing procedure for all Na\(_n\) and Na\(_n^+\) clusters shown here, as well as for Mg\(_n\) and Mg\(_n^+\) up to \( n = 15 \).

5. All found configurations were checked for congruency, i.e., for being identical up to rotations and/or translations. It turned out that all structures with an energy difference greater than 10\(^{-4}\) Ry per electron were isomers. In four cases we have also found incongruent configurations with an energy difference of less than 10\(^{-3}\) Ry per electron. Two of these will be discussed below.

To estimate the discretization error, we have also calculated, for some sample clusters, the total energy while...
rigidly moving and rotating the ions in different directions in the simulation box. For all clusters, the discretization error is around $10^{-5}$ Ry, which is certainly much smaller than the uncertainty implicit to the local density approximation.

In order to find a locally stable configuration, we have typically carried out about 1000 Langevin moves, slowly decreasing the artificial temperature $T = 1/(k_B \beta)$. These were followed by several hundred steepest descent moves. Therefore, each locally stable configuration shown here involved between 1000 and 2000 LDA calculations for the cluster under consideration. The diffusion algorithm described above is particularly efficient for such a strategy, because it iteratively improves a given set of initial wave functions, and thus profits from good starting values. Since the ions are moved only very little during one annealing step, the wave functions do not change much, and the diffusion algorithm for subsequent steps converges within just a few iterations.

3 Results

3.1 Na and Na$^+$ clusters

Na$^-$ and Na$^+_n$ clusters are the most frequently studied type of metallic clusters, for a recent review see Ref. [12]. We have examined these systems basically to highlight the differences between Na$^-$ and Mg$^-$ clusters. We have performed (S)DFT calculations for small Na$^-$ and Na$^+_n$ clusters up to $n = 10$. The calculations were carried out on a regular, Cartesian real-space grid with $64^3$ mesh points and a resolution of 0.5 $a_0$, where $a_0$ is the Bohr radius. We have determined that this is the coarsest discretization that is permitted to get reliable results. Our discretization corresponds to an energy cutoff of 537 eV in plane-wave calculations.

All calculations in this section have been carried out using the empirical pseudopotentials of both Fiolhais et al. [9] and Kümml et al. [10], for the purpose of testing the sensitivity of the results to the pseudopotential used. In one case, we have additionally used norm-conserving non-local pseudopotentials of the Troullier-Martins type [11], see Fig. 4.

3.1.1 Energetics

The binding energy for neutral and singly charged clusters is defined by

$$E_{b,n} = nE_1 - E_n,$$
$$E_{b,n}^+ = (n-1)E_1 + E_1^+ - E_n^+,$$

where $E_1$ and $E_n$ are the ground state energies of a single Na atom and a Na$^-$ cluster, respectively, and $E_1^+$ and $E_n^+$ are their counterparts for the charged clusters.

Figs. 1 and 2 show the binding energy per atom for Na$^-$ and Na$^+_n$ clusters in comparison with previous work [12,46,47,48], where we find generally good agreement. For neutral clusters we have found that the pseudopotential proposed by Fiolhais et al. [9] and that of Kümml et al. [10] give almost identical results. For charged clusters, the difference in the binding energy due to different pseudopotentials is comparable to the discrepancy between different calculations.

Consistent with earlier work, we observe a particularly high stability for Na$_3$, Na$_4$, Na$_5^+$ and Na$_9^+$, where the binding energy per atom is higher than the one of the cluster with one additional atom. This is known to be due to electronic shell closure and predicted by ellipsoidal jellium models [49]. We also observe an additional peak for Na$_5^+$ which can not be explained by shell closures. This peak is consistent with earlier theoretical calculations [50]; it has also been observed in Na$_{5}^{+}$ fragmentation experiments [51]. It is the onset of an even-odd alternation which has been attributed to electron pairing effects [52].
### 3.1.3 Kohn-Sham energies

The Kohn-Sham energies of the ground state structures for Na\(_n\) and Na\(^{+}\)\(_n\) are depicted in Figs. 5 and 6. For odd electron numbers we have used the LSDA, which implies that electrons with different spins can have different wave functions and energy eigenstates. The lowest states in these figures correspond to the 1s-states. The 1p-states are separated by a rounded gap and can be clearly identified, as well as the onset of the 1d-states.

The energy levels show a good overall agreement with the single-particle levels predicted by the Clemenger-Nilsson model \[\text{[53], see Fig. 5(a) in Ref. 19.}\] This indicates that ellipsoidal jellium models give a good qualitative description of Na clusters. One notable difference is Na\(_8\): While clusters with closed shells usually are spherically symmetric and thus show degenerate \(p\)-states in jellium models, this degeneracy has been lifted in our calculation. This is a result of the symmetry breaking due to the ion cores, and has been observed previously, see, e.g., Fig. 5(d) in Ref. 19.

The Clemenger-Nilsson model predicts shell closures for Na\(_2\), Na\(_3\), Na\(_4\) and Na\(_6\) \[\text{[19,53].}\] Correspondingly, the neighboring clusters show a significantly decreased gap in at least one spin channel in Figs. 5 and 6. In addition to these shell closures, we also observe the even-odd alternation attributed to the electron pairing effects mentioned above \[\text{[52].}\] Due to this effect, also Na\(_6\) and Na\(_8\) show a particularly large gap.

### 3.2 Mg and Mg\(^{+}\) clusters

The focus of our work is the calculation of structures and energetics of Mg\(_n\) and Mg\(^{+}\)\(_n\) clusters. We have again used the procedure outlined in Sec. 2.5 to find ground states and low-lying isomers of Mg\(_n\) and Mg\(^{+}\)\(_n\) clusters up to \(n = 30\). The ion cores of the Mg atoms have been described by the local potentials of Ref. 9.

Due to the shorter range of the Mg pseudopotentials compared to those for Na, all calculations have been performed on a regular, Cartesian real-space grid with 96\(^3\) mesh points and a resolution of 0.375 \(a_0\). This corresponds to an energy cutoff of 954.5 eV in a plane-wave calculation.

### Table: Na\(_n\) and Na\(^{+}\)\(_n\) ground state structures

| \(n\) | \(E_{\text{b}}/n\) (Ry) | \(d_{\text{min}}\) \((a_0)\) | \(d_{\text{max}}\) \((a_0)\) |
|---|---|---|---|
| 2 | -0.024940 | 5.706716 | 6.380787 |
| 3 | -0.021711 | 6.175658 | 6.717198 |
| 4 | -0.031481 | 6.062901 | 6.889472 |
| 5 | -0.033695 | 6.437029 | 6.717198 |
| 6 | -0.039365 | 5.807587 | 6.479877 |
| 7 | -0.041664 | 6.105434 | 6.889472 |
| 8 | -0.045404 | 6.330009 | 6.889472 |
| 9 | -0.043287 | 6.494340 | 6.889472 |
| 10 | -0.045243 | 6.530012 | 6.889472 |

### Fig. 3.

(color online) Ground state configurations of neutral Na\(_n\) and singly charged Na\(^{+}\)\(_n\) clusters up to \(n = 10\). The results reported here were obtained using the potential of Fiolhais et al. \[\text{[9].}\] Note that we show, in the case Na\(_4\), the rhomboid isomer. Local pseudopotentials predict an additional distorted configuration slightly lower in energy, see Fig. 2. \(E_{\text{b}}/n\) is the binding energy per atom, \(\langle d\rangle\), the average nearest neighbor distance, and \(d_{\text{min}}\) and \(d_{\text{max}}\) are the smallest and largest nearest neighbor distances, respectively.

### Fig. 4.

(color online) Ground state configurations of Na\(_4\). Left pane: “distorted” rhomboidal configuration which is found as the ground state with both local pseudopotentials. Right pane: Symmetric configuration, found as slightly higher-lying isomer with local potentials (energy difference: +3.96 \cdot 10^{-4} Ry). For non-local Troullier-Martins pseudopotentials, the distorted configuration is not stable, and the symmetric configuration shown right is the ground state structure.
A comment is in order concerning the expected accuracy of the applied theory. This can be assessed by comparing predictions for small systems with results obtained by more elaborate methods. Refs. [18] and [54], for instance, compare the bond lengths of Mg$_3$ and Mg$_4$ obtained from coupled cluster (CC) and DFT calculations. The CC calculations included single and double excitations as well as perturbative triples [CCSD(T)], the DFT calculations were all-electron calculations using the BP86 correlation functional. The results of both methods agree with ours within a few percent. This is certainly better than expected because the pseudopotentials used in our work have been designed to reproduce bulk properties.

To safely bracket the regime where a non-metal to metal (NMM) transition has been proposed [13-15], we have calculated structures up to $n = 30$. The binding energy for neutral and singly charged clusters is defined in Eq. (11), where $E_1$ and $E_n$ are the ground state energies of a single Mg atom and a Mg$_n$ cluster, and $E_1^+$ and $E_n^+$ their counterparts for the charged clusters, respectively. By repeating the annealing procedure with different initial configurations, we have also calculated isomers for ion numbers $n \leq 15$; for larger clusters the number of isomers grows rapidly and identifying all of them becomes extremely time consuming.

Figures 7 and 8 show our results for the binding energy per atom, $E_b/n$, of Mg$_n$ clusters in comparison with earlier calculations as cited in the legend.

### 3.2.1 Energetics

For a quantitative assessment of cluster stability, we turn our attention to the possible fragmentation channels. A Mg$_n$ cluster can dissociate into two smaller clusters of sizes $n - m$ and $m$. The fragmentation energies are defined
Fig. 8. (color online) Binding energy per atom, $E_{b,n}^+/n$, of Mg$_n^+$ clusters in comparison with earlier calculations as cited in the legend.

\[
\Delta E_n \equiv \max_{1 \leq m < n} \left[ E_{b,n-m} + E_{b,m} - E_{b,n} \right],
\]

\[
\Delta E_n^+ \equiv \max_{1 \leq m < n} \left[ E_{b,n-m}^+ + E_{b,m}^+ - E_{b,n}^+ \right].
\]

(12)

If this quantity is negative, the cluster is stable against spontaneous fragmentation. Nevertheless, for each cluster, we denote the channel with the highest fragmentation energy as the preferred fragmentation channel, even if the cluster is stable. Figs. 9 and 10 show the dependence of the binding energy on cluster size. We found that all Mg and Mg$^+$ clusters are stable. The preferred fragmentation channel for neutral clusters is always

\[
\text{Mg}_n \rightarrow \text{Mg}_{n-1} + \text{Mg}_1.
\]

(13)

For singly ionized clusters it is, correspondingly,

\[
\text{Mg}_n^+ \rightarrow \text{Mg}_{n-1}^+ + \text{Mg}_1.
\]

(14)

for all cluster sizes. This is due to the monotonic increase of the binding energy with the number of atoms, in contrast to Na clusters, which often decay as Na$_n \rightarrow$ Na$_{n-2} +$ Na$_2$.

Another criterion for cluster stability \[10\] involves the second energy difference,

\[
\Delta_2 E_n^{(+)} \equiv E_n^{(+)} - 2E_{n-1}^{(+)} + E_{n-1}^{(+)}.
\]

(15)

where the superscript $^{(+)}$ indicates that the formula applies to both neutral and charged clusters. Eq. 15 can be understood as a discretized second derivative of the electronic energy with respect to the ion number. If $\Delta_2 E_n^{(+)} > 0$, then Mg$_n^{(+)}$ is stable with respect to disproportionation of two Mg$_{n-1}^{(+)}$ clusters into Mg$_{n-1}^{(+)}$ and Mg$_{n+1}^{(+)}$. A higher value indicates a more stable cluster. The evolution of these quantities with cluster size among some representative results found in the literature are shown in Figs. 11 and 12 respectively.

We can use both the fragmentation energies and the second energy differences to identify extraordinarily stable clusters. To find those, we look for clusters that show a distinct minimum in $\Delta E_n^{(+)}$ and a distinct maximum in $\Delta_2 E_n^{(+)}$ in the region where $\Delta_2 E_n^{(+)} > 0$. This procedure suggests that neutral Mg$_n$ clusters with 4, 7, 10, 17, 21, 23 and 27 atoms are particularly stable. For the ionized Mg$_n^+$ clusters, the most stable sizes are 5, 8, 10, 17, 20, 23 and 27, respectively. Diederich et al. 13 have measured the abundance of Mg$_n^+$ clusters grown in ultracold liquid helium nanodroplets using mass spectroscopy. They report,

Fig. 9. (color online) Fragmentation energies of Mg$_n$ clusters in the energetically preferred channel, $\Delta E_n$, for neutral Mg$_n$ clusters up to $n = 30$, see Eq. 12. Results of some earlier works are shown as cited in the legend.

Fig. 10. (color online) Fragmentation energies of Mg$_n^+$ clusters in the energetically preferred channel for singly ionized Mg$_n^+$ clusters, $\Delta E_n^{(+)}$, up to $n = 30$, see Eq. 12. Results of some earlier works are shown as cited in the legend.
in the area of cluster sizes covered here, distinct maxima in the abundance distribution at clusters sizes 5, 10 and 20, as well as a local maximum at 8. All of these “magic numbers” are consistent with the stable cluster sizes predicted by the above procedure.

The clusters Mg_{14}, Mg_{27}, and Mg_{29}+, which are also predicted to be particularly stable by our analysis, do not show up as abundance maxima in the experiment. Two of these clusters, Mg_{25} and Mg_{29}+, seem to have a somewhat peculiar geometrical structure, see Sec. 3.2.2

The evolution of the adiabatic ionization energies,

\[ E_{\text{ion}, n} \equiv E_{n}^+ - E_{n}^- , \]

with cluster size is shown in Fig. 13. The almost monotonically decreasing values are in good agreement with previous calculations [55,56].

3.2.2 Geometric structure

Fig. 14 shows the ground state geometries of the neutral and charged Mg_{n} clusters up to n = 11. Displaying the individual ion positions for larger clusters does not provide much useful information, these positions can be found in Ref. [58].

To examine the structure of larger clusters, we look at the pair distribution function of the ions. The classical two-body density of the ion cores,

\[ \rho_2(\mathbf{r}, \mathbf{r}') = \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{R}_i)\delta(\mathbf{r}' - \mathbf{R}_j) , \]

contains the most useful information about the geometric structure of the cluster. To reduce the number of variables, we rewrite \( \rho_2(\mathbf{r}, \mathbf{r}') \) in terms of the relative coordinate \( \mathbf{x} = \mathbf{r} - \mathbf{r}' \) and the center of mass coordinate and average over the center of mass coordinate as well as over the remaining angular degrees of freedom. This defines the so-called average radial distribution function \( \tilde{g}_n(x) \),

\[ \tilde{g}_n(x) = \frac{1}{4\pi x^2 \rho_0 n} \sum_{i \neq j} \delta(x - |\mathbf{R}_i - \mathbf{R}_j|) , \]

where \( \rho_0 \) is the average bulk density. This procedure yields the exact pair distribution function for homogeneous systems. Finally, to obtain a smooth function, we have broadened the distribution of pair distances \( x \) by a Gaussian of width \( \epsilon \),

\[ \tilde{g}_{n, \epsilon}(x) = \frac{1}{4\pi \sqrt{2\pi \epsilon^2 \rho_0 n}} \sum_{i \neq j} e^{-\frac{1}{2\epsilon^2}(x - |\mathbf{R}_i - \mathbf{R}_j|)^2} . \]

For small \( \epsilon \), Eq. (19) is identical to the discretized expression in Eq. (18).
The peaks in $\bar{g}_{n,\epsilon}(x)$ correspond to a high probability of finding two atoms at a distance $x$ and, in the bulk limit, correspond to the sequence of $n$-th nearest neighbor distances $\xi$. For face-centered cubic (fcc) and hexagonal close packed (hcp) structures, the ratios between first and second, and first and third nearest neighbor distances are

$$\xi_2 : \xi_1 = \sqrt{2}, \quad \xi_3 : \xi_1 = \sqrt{3} \quad \text{(fcc and hcp)}.$$  \hspace{1cm} (20)

The pair distribution functions $\bar{g}_{n,\epsilon}(x)$ for a few selected neutral and singly ionized Mg clusters are shown in Figs. 15 and 16. While Mg$_{30}$ is still far away from the bulk limit, one cannot nevertheless clearly identify a sequence of peaks in the plot of $\bar{g}_{30,\epsilon}(x)$. In this case, we have determined the positions of these peaks to be $\xi_2 = 6.275 a_0$, $\xi_3 = 8.375 a_0$ and $\xi_3 = 10.725 a_0$, respectively. The corresponding ratios of peak positions are

$$\xi_2 : \xi_1 = 1.34 (-5.24\%), \quad \xi_3 : \xi_1 = 1.71 (-1.27\%).$$  \hspace{1cm} (21)

where the values in parentheses give the error relative to the known ratios for the bulk fcc and hcp lattices as given in Eq. (20). From our calculations one would therefore conclude that magnesium clusters approach, with increasing cluster size, either fcc or hcp structure. The Mg$_{30}$ cluster is still too small to reliably extract a fourth peak from $\bar{g}_{30,\epsilon}(x)$, which would allow to distinguish between these two structures. However, up to the cluster sizes taken into account here, our results are consistent with the known hcp symmetry of bulk magnesium.

We finally draw attention to another remarkable piece of information that can be gained from Figs. 15 and 16. When comparing the average pair distribution functions for the different clusters in the range from 8$a_0$ to 10$a_0$, it is evident that $\bar{g}_{n,\epsilon}(x)$ is zero for the clusters Mg$_{8,14}^{+}$,
Mg$_{23}$ and Mg$_{23}^+$, while it is non-zero for all other clusters examined here. It can be concluded that those clusters do have a geometric structure that is qualitatively different from that of the other "magic" clusters.

From the geometric configurations of the Mg$_n$ clusters we can calculate the average nearest neighbor distance $\langle d \rangle_n$ and the smallest and largest nearest neighbor distances $d_{\text{min},n}$ and $d_{\text{max},n}$, respectively. The numerical values for these quantities up to a cluster size of $n = 11$ are given in Fig. 14. The evolution of $\langle d \rangle_n$ with cluster size for both neutral and singly ionized clusters is shown in Fig. 17 together with results from Refs. [55] and [56]. The dotted line in this figure marks the bulk limit of $\langle d \rangle = 6.07$ a$_0$ for solid magnesium. Evidently, at $n = 30$ both neutral and charged clusters are already close to that limit.

### 3.2.3 Kohn-Sham energies

The Kohn-Sham levels of the ground state structures of Mg$_n$ and Mg$_n^+$ are shown in Figs. 18 and 19. For the Mg$_n^+$ clusters, the LSDA has been used; we therefore show the energy levels for both spin channels in separate plots.

In contrast to the HOMO-LUMO gaps of the sodium clusters shown in Figs. 5 and 6, the gaps of the magnesium clusters do not show strong signs of electronic shell closures: The gap decreases rather monotonically with cluster size; the pronounced "zigzag" structure of the HOMO and LUMO levels found in sodium is missing. This is an indication that small Mg clusters are more covalently bound and electrons are more localized in comparison to sodium clusters. This prediction is confirmed by the respective electron densities, see Sec. 8.2.4.

In a bulk system, the closing of the HOMO-LUMO gap can be considered as a sign of an NMM transition. In finite-sized systems like clusters, the gap between energy levels is always finite, and the answer to the question whether a material is a metal or not depends on

\[ \langle d \rangle_n \text{ [a$_0$]} \]

\[ 30 \quad 25 \quad 20 \quad 15 \quad 10 \quad 5 \quad 0 \]

}\]

\[ Kohn − Sham energy levels \text{ [Ry]} \]

\[ 0.0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \]

\[ 0.0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \]

\[ Kohn − Sham energy levels (up) \text{ [Ry]} \]

\[ Kohn − Sham energy levels (down) \text{ [Ry]} \]

\[ 0.0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \]

\[ Kohn − Sham energy levels (down) \text{ [Ry]} \]

\[ Kohn − Sham energy levels (up) \text{ [Ry]} \]
its temperature [17]. Specifically, a temperature of 300 Kelvin corresponds to roughly $1.9 \times 10^{-3}$ Ry. The calculated HOMO-LUMO gaps shown in Figs. [18] and [19] are on the order of 0.02–0.10 Ry. Therefore, Mg clusters with up to 30 atoms are not metallic by this criterion. Note that the LDA is known to systematically underestimate band gaps (see, e.g., Ref. [59]), and is thus erring on the side of caution when predicting non-metallicity.

At first glance, this conflicts with Refs. [14,15,16], where the NMM transition has been observed for Mg clusters in helium at around $n = 20$. However, Refs. [18,19] suggest that the observed NMM transition most likely refers to negatively charged Mg$_{n}^{-}$ clusters used in these experiments and thus does not disagree with our findings.

3.2.4 Electron density

The most telling documentation of the difference between Na$_n$ and Mg$_n$ clusters is the electron density. In Figs. 20 and 21 we show, as examples, contour plots of the electron density of the Na$_7$ and Mg$_7$ ground state configuration in the symmetry plane. We have chosen these examples because their ionic configuration is very similar, see Figs. 3 and 13.

From Figs. 20 and 21 it is clear that the electrons in a Na$_7$ cluster are much more delocalized than in a Mg$_7$ cluster. If there were an NMM transition in the range of cluster sizes under consideration here, one would expect a delocalization of electrons and a much broader electron density for larger clusters. In Fig. 22 we show therefore a contour plot of the electron density in a Mg$_{30}$ cluster. The electrons are just as strongly localized as in Mg$_7$, indicating that neutral clusters have, at that ion number, not yet undergone an NMM transition.

3.2.5 Isomers

Tables 1 and 2 show the binding energies per atom, $E^{(+)}_{b,n}$, for the ground states of neutral Mg$_n$ and singly charged
Mg$_n$ clusters, together with the differences in binding energy per atom of identified isomers to the corresponding ground state.

A remarkable feature of these results can be seen in Table 2. For all clusters between Mg$_7^+$ and Mg$_{10}^+$, the lowest-lying isomer is energetically almost degenerate with the ground state. Figs. 23 and 24 show the corresponding geometric structures for Mg$_7^+$ and Mg$_{10}^+$, respectively. In the case of Mg$_7^+$, see Fig. 23 both the ground-state and the lowest-lying isomer are composed of the same Mg$_7^+$ core structure, with the additional atom added at two different positions. For Mg$_{10}^+$, shown in Fig. 24 the situation seems to be more complicated. Here the atom positions and bonding angles for the two configurations are considerably different.

### 4 Conclusion

We have presented a systematic study of neutral and singly charged Na$_n$ and Mg$_n$ clusters. We have employed a real-space algorithm that is particularly well suited for the problem at hand: It allows a fine coordinate-space resolution that is able to deal with even small annealing steps. The process is iterative and profits from the knowledge of accurate solutions of near-by configurations. We found, during the annealing process, that the HOMO-LUMO gaps are indeed very sensitive to the details of the ground state structure. Thus, the last annealing steps were of the order of $10^{-4} \hbar_0$. We have verified the numerical stability of our procedure by moving and rotating the cluster with respect to the coordinate space mesh. The total energy had uncertainties comparable to what is gained during the final annealing steps, but the relative energies between neighboring configurations were independent of the precise location and orientation of the cluster.

The relatively strongly localized electron density in Mg clusters also suggests that a simple jellium model can not describe the cluster properties accurately. In contrast to alkali clusters in general, where the delocalized electrons dominate the cluster structure, the geometric symmetry seems to be more important for Mg clusters. The highly symmetric Mg$_{11}$ cluster has, for instance, only a slightly higher binding energy per atom than Mg$_{10}$, for which the

| Mg$_n$ | $E_{n,n}/n [\text{Ry}]$ | $b [10^{-3} \text{Ry}]$ | $c [10^{-3} \text{Ry}]$ | $d [10^{-3} \text{Ry}]$ |
|-------|---------------------|-------------------|-------------------|-------------------|
| Mg$_2$ | 0.048724            |                   |                   |                   |
| Mg$_3$ | 0.053346            |                   |                   |                   |
| Mg$_4$ | 0.052536 -1.382     |                   |                   |                   |
| Mg$_5$ | 0.053102 -0.902     |                   |                   |                   |
| Mg$_6$ | 0.052759 -1.296 -1.622 +2.235 |
| Mg$_7$ | 0.051013 -0.013 -0.182 |
| Mg$_8$ | 0.051870 -0.008 -0.892 |
| Mg$_9$ | 0.051520 -0.024 -0.214 |
| Mg$_{10}$ | 0.053659 -0.049 -0.485 |
| Mg$_{11}$ | 0.053859 -0.333 -1.496 |
| Mg$_{12}$ | 0.053125 -0.304 -1.051 |
| Mg$_{13}$ | 0.053817 -0.184 -0.379 -0.425 |
| Mg$_{14}$ | 0.054982 -0.335 -0.375 -0.577 |
| Mg$_{15}$ | 0.055399 -0.268 |
jellium model predicts an electronic shell closure. Nevertheless, the stability analysis depicted in Fig. 9 shows that Mg$_{10}$ is still more stable than Mg$_{11}$. This is different for Mg$_{20}$ and Mg$_{21}$: The jellium model predicts a shell closure for Mg$_{20}$, but our calculations show that Mg$_{21}$ is slightly more stable than Mg$_{20}$.

Because Mg$_{n}$ and Mg$_{n}^{+}$ clusters with up to 30 do not show closing HOMO-LUMO gaps, we conclude that these clusters are not metallic. This is consistent with the findings of Refs. [13,19] that the observed NMM transition for Mg clusters in helium at around $n = 20$ is most likely refers to the negatively charged Mg$_{n}^{-}$ clusters used in the corresponding experiments.

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