

NeNa

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Zusammenfassung

Zugsamenfassung: Ziel, Methoden, Ergebnisse, Schlussfolgerungen

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Abkürzungsverzeichnis

LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
HF	Hartree-Fock
BSSE	Basis Set Superposition Error
fcc	face-centered-cubic

Symbolverzeichnis

Symbol	Bedeutung	Einheit
B	magnetische Flussdichte	T
D	Elektrische Flussdichte	A s m^{-2}

1 Einleitung

Einleitung: Wieso sollte diese Arbeit gelesen werden?

2 Aufgabenstellung

We are here trying to calculate optical absorption spectra with vasp. The atomic configuration is a cavity inside a neon crystal that was proposed to be filled with either a single sodium atom or two sodium atoms (a sodium dimer). Now the first step was to find configurations of cavities, i.e. how many neon atoms will be replaced by an inserted sodium atom and subsequently by a sodium dimer. This substitution number will be denoted as S in the following thesis. For these specific configurations the optical absorption spectra will be calculated and compared with the experiment.

3 Theory

3.1 Statistical Mechanics

First we consider the system of the crystal of Neon Atoms as a canonical ensemble, this means it will be described under the assumption of an infinitely large heat bath by Boltzmann statistics. The probability distribution of members of the ensemble will then be

$$p(\vec{\mathbf{q}}, \vec{\mathbf{p}}) = \frac{e^{-\beta H(\vec{\mathbf{q}}, \vec{\mathbf{p}})}}{\int \dots \int e^{-\beta H(\vec{\mathbf{q}}, \vec{\mathbf{p}})} d^{3N} \vec{\mathbf{q}} d^{3N} \vec{\mathbf{p}}}, \quad (3.1)$$

with N being the number of particles.

Now an ensemble is to be understood as many fictional copies of the same system representing the states that a system will explore when propagating in time according to Hamilton's equation of motion. The ensemble distribution represents the relative number of times that an ergodic system will come by a given state after an infinite amount of time has passed. Now for a crystal in principle this still holds. At low temperatures though the phase space that is being explored can be abstracted in such cases. The reason is that the system will for a given finite time usually explore only nearby points in the phase space. This is the crystal configuration but allowing for dynamics such as lattice vibrations and thermal movement of the atoms with respect to their lattice site. So for a given initial point in phase space the system will mostly explore its proximity until it probabilistically jumps to another volume of phase space whose proximity then will be explored for some further time. Now this means the systems lattice configuration has changed which at low but non zero temperature should be reasonable. We now consider these volumes of phase space (being approximately confined regions, i.e. configurations of e.g. a crystalline structure) to be discrete states that the system can be in. So our canonical distribution now is a discrete one, each state representing such a configuration volume. What's left is to figure out what state of the still continuously possible states inside will be used to represent each configuration. We in this work will use the state $(\vec{\mathbf{q}}_{0i}, \vec{\mathbf{p}}_{0i})$ that locally minimizes $H(\vec{\mathbf{q}}, \vec{\mathbf{p}})$. Such a minimum can be found by employing a relaxation calculation in [LAMMPS](#). The Boltzmann distribution now follows to be:

$$p(\vec{\mathbf{q}}_{0i}, \vec{\mathbf{p}}_{0i}) = \frac{e^{-\beta H(\vec{\mathbf{q}}_{0i}, \vec{\mathbf{p}}_{0i})}}{\sum_n e^{-\beta H(\vec{\mathbf{q}}_{0n}, \vec{\mathbf{p}}_{0n})}}. \quad (3.2)$$

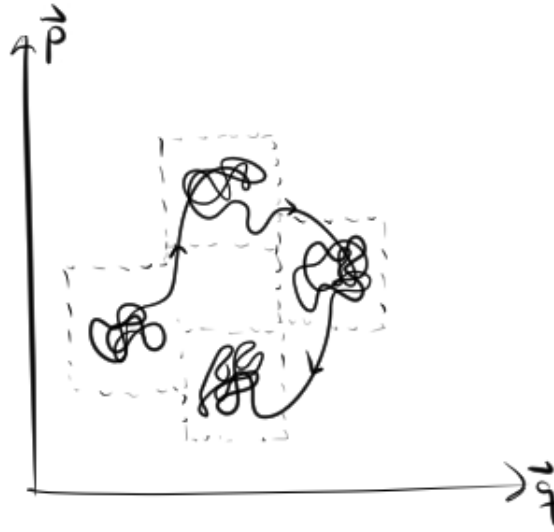


Figure 3.1: state evolution $(\vec{q}(t), \vec{p}(t))$ through 6N-dimensional phase space

grand canonical ensemble with two chemical components

sub term of grand canonical ensemble with only ne1 and ne2

Explanation for cohesive energy

3.2 Relaxation in LAMMPS

relaxation theory form lammmps described in [1] Bitzek, Koskinen, Gahler, Moseler, Gumbusch, Phys Rev Lett, 97, 170201 (2006). Testcite Griffiths[2]

3.3 Simulated Annealing

The object that is being annealed is a state vector containing binary information for every lattice site. It refers to the ideal static lattice of the neon structure. A positive value or 1 refers to an atom being present in the initial structure and a negative value or 0 means the neon atom is vacant at this site. So every digit of the binary state refers to a certain specific lattice site. The energy functional of the annealing process will be the energy after minimization (i.e. relaxation) of the above described state vector. This state vector therefore refers to an initial pre-relaxation configuration where sites are simply removed with [LAMMPS](#).

Energy functional contains cohesive Energy/chemical potential, not just hamiltonian!!

Listing 3.1: Simulated annealing algorithm

```
1 stateVector = [1,1,1,1,1,1,1,1,1,1,1,1,1,1]
2 alpha = (Tend / Tstart) ** (1 / N)
3
4 for i in N:
5     T = Tstart * (alpha**i)
6
7     n = randomInt(1,len(stateVector))
8     stateVector[n] = 1 - stateVector[n]
9
10    stateVectorOld = stateVector
11
12    EOld = minimizeEnergy(stateVectorOld)
13    E = minimizeEnergy(stateVector)
14
15    if E >= EOld:
16        stateVector = stateVectorOld
17    elif random(0,1)<=exp(-1/T*(E-EOld)):
18        stateVector = stateVectorNew
19
20 S = 1
21 for site in stateVector:
22     if site == 0:
23         S += 1
```

3.4 Symmetry optimization

In the case of a single sodium atom inserted in the neon crystal the highly symmetrical structure was exploited to reduce redundant minimization calls in the annealing routine, by identifying symmetrically equivalent structures and caching them. Applying rotation and reflection matrices of the octahedral symmetry group to a single configuration was used to quickly create all equivalent configurations. By sorting them lexicographically and picking e.g. the first, one ensures every redundant set of configurations is always represented by the same configuration.

3.5 DFT optical spectra

Listing 3.2: lexicographically sorting point group symmetries

```
1 equivs = np.transpose(np.einsum("klj,ij", oh_group, pos), (1, 0, 2))
2
3 for k in range(equivs.shape[0]):
4     equivs[k] = equivs[k][np.lexsort(equivs[k].T[:,-1])].copy()
5     sorting_idx = np.lexsort(
6         np.transpose(equivs, (2, 1, 0)).reshape(pos.size, oh_group.shape[0])
7     )
8     pos = equivs[sorting_idx[0], :, :]
```

4 Finding Minima of Neon Replacements

4.1 Pair Potential Interaction

4.1.1 Hartree-Fock (HF) equations

We start with the pair potentials of Ne-Ne, Ne-Na and Na-Na to mimic the interaction of long distance van der Waals + short distance repulsion forces. The pair potentials have been calculated using a HF self consistent field cycle by varying the atom distance. Now selfconsistently solving the equations:

$$\left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_0} - \frac{e^2}{4\epsilon_0} \sum_{\nu,\sigma}^{(\mu\sigma) \neq (\nu\sigma)} \iiint_{\mathbb{R}^3} \frac{\varphi_{\nu\sigma'}(\tilde{\vec{r}})}{\|\vec{r} - \tilde{\vec{r}}\|} d^3\tilde{\vec{r}} - \hat{A}_{\mu\sigma}(\vec{r}) \right] \varphi_{\mu\sigma}(\vec{r}) = \varepsilon_{\mu\sigma} \varphi_{\mu\sigma}(\vec{r}), \quad (4.1)$$

with $\hat{A}_{\mu\sigma}$ being the exchange correlation term leads to the eigenenergies $\varepsilon_{\mu\sigma}$. Since HF minimizes a slater determinant, the energies correspond to the factors of the slater product state, meaning the systems energy is the sum of the energy of the single electrons. From that, to get the actual energy of the whole system, one needs to remove inter-electron repulsion and exchange correlation from the sum of all eigenenergies $\varepsilon_{\mu\sigma}$:

$$E_{HF}^0 = \sum_{\mu,\sigma} \varepsilon_{\mu\sigma} - \frac{1}{2} \sum_{\substack{\mu,\nu \\ \sigma,\sigma'}}^{(\mu\sigma) \neq (\nu\sigma)} \left[C_{\mu\sigma}^{\nu\sigma'} - A_{\mu\sigma}^{\nu\sigma} \delta_{\sigma\sigma'} \right] \quad (4.2)$$

with $C_{\mu\sigma}^{\nu\sigma'}$, $A_{\mu\sigma}^{\nu\sigma}$ being defined as:

$$C_{\mu\sigma}^{\nu\sigma'} = \frac{e^2}{4\pi\epsilon_0} \iint \frac{|\varphi_{\mu\sigma}(r)|^2 |\varphi_{\nu\sigma'}(r')|^2}{|r - r'|} d^3r d^3r', \quad (4.3)$$

$$A_{\mu\sigma}^{\nu\sigma} = \frac{e^2}{4\pi\epsilon_0} \iint \frac{\varphi_{\mu\sigma}^*(r) \varphi_{\nu\sigma}^*(r') \varphi_{\mu\sigma}(r') \varphi_{\nu\sigma}(r)}{|r - r'|} d^3r d^3r'. \quad (4.4)$$

Since solving the HF equations in real space is too costly one restricts the variations to coefficients of a superposition of fixed basisvectors. These lead to the Roothaan-Hall equations, which are a discrete Matrix representation of the HF equations:

$$\mathbf{FC} = \mathbf{SC}\epsilon, \quad (4.5)$$

with ϵ being a diagonal matrix of single particle energies on the diagonal, \mathbf{S} the basis overlap matrix, \mathbf{C} the coefficient matrix and finally \mathbf{F} the Fock operator.

4.1.2 Moeller-Plesset Perturbation

-go from pair HF to moller plesset

4.1.3 Basis Set Superposition Error (BSSE)

Now the the superpositions of a fixed basis leads to the BSSE. These errors are being corrected for by using 'ghost calculations', essentially the same calculation with one atom being removed (i.e. the extended two atom centered basis stays the same). This means the basis will have access to the second electron states, but the nucleus and additional electrons are not accounted for. These 'ghost energies' will then subsequently be removed from the HF approximation to correct for the BSSE. This is know as the counterpoise-corrected interaction energy formula or Boys–Bernardi method:

$$E_{\text{int}}^{\text{CP}}(R) = E_{AB}(R) - E_A^{\text{ghost}}(R) - E_B^{\text{ghost}}(R). \quad (4.6)$$

4.1.4 Interpolation

-explain exact interpolation
-paper citation where brute force plot shows up as well
-which basis is being used in the roothaan equations
-explain setup of calculation with ball being carved out
-maybe here explain the nearest neighbours
lammmps gets linear interpolation
-since plot is in priniple linearly interpolated this is the exact pair interactins that lammmps will read

4.2 Geometric LAMMPS Setup

The simulation models a finite spherical cluster of atoms extracted from a bulk face-centered cubic lattice. To balance computational efficiency with physical realism, the system is partitioned into two concentric spherical regions defined in units of the lattice constant. The inner spherical region, with radius n_{inner} contains atoms that are free to move and evolve dynamically. This region represents the core of the cluster where

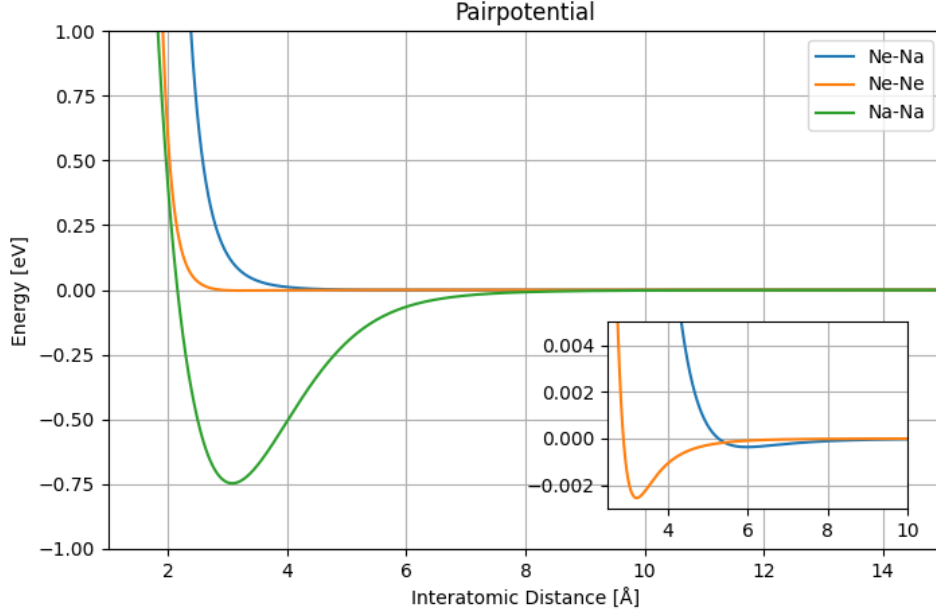


Figure 4.1: Plots of interpolations of pair potentials of Ne-Ne, Na-Na, Ne-Na calculated with Moeller Plesset 2 perturbation theory.

physical process and in this case the energy minimization via a relaxation calculation of [LAMMPS](#) takes place.

Surrounding this core is an immobilized shell with thickness n_{outer} . Atoms within this outer shell are constrained by setting their forces to zero, effectively fixing them in space. This fixed shell acts as a rigid boundary that suppresses surface effects and mimics the presence of an extended bulk lattice, thereby reducing finite size artifact in the dynamics of the inner region.

Consequently the total cluster is confined within a spherical domain of radius $R_{tot} = (n_{inner} + n_{outer}) \cdot a$ with a being the lattice constant of the pure neon face-centered-cubic ([fcc](#)) lattice.

Technically the simulation is defined as a cubic volume large enough to contain the entire spherical cluster, with half-length at least R_{tot} . For the relaxation mechanics atomic positions are set according to [4.2](#) on a perfect [fcc](#) lattice no matter their role (sodium defect, fixed neon, dynamic neon) as long as they are inside the cutoff radius R_{tot} . This approach is commonly employed in molecular dynamics studies to simulate nanoparticles or finite clusters embedded in bulk-like surroundings.

The centered red dots in [4.2](#) represent sodium atoms. They represent the initial pre-relaxation positions of sodium inside the dynamic inner sphere. These initial positions

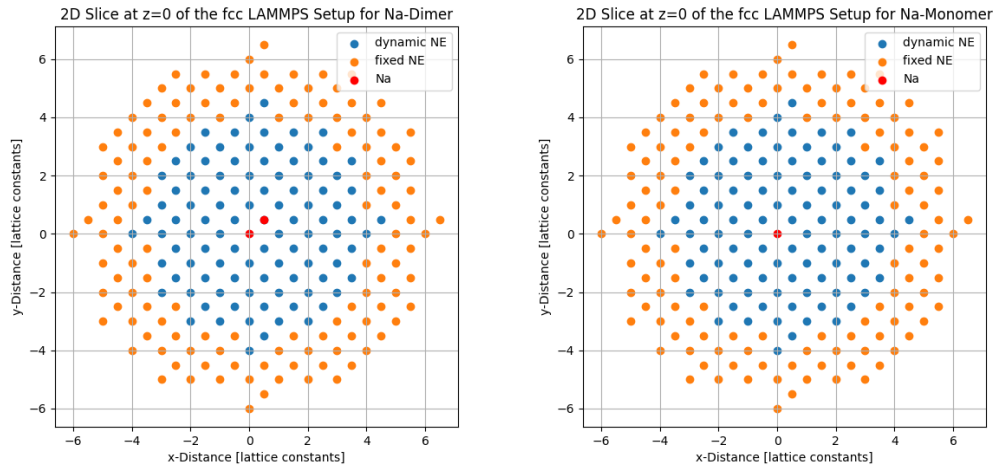


Figure 4.2: Initial setup for the [LAMMPS](#) relaxation. Only the inner blue sphere is allowed to relax, forces on the orange atom positions are overridden to 0.

are the same for every relaxation step of the simulated annealing. Note that the minimum energy of the pair-potential in [4.1](#) is roughly at 3.1 \AA which is roughly the nearest neighbour distance

$$R \tag{4.7}$$

in the neon [fcc](#) lattice. We therefore put the second sodium atom in the dimer calculations at the nearest neighbour lattice site.

4.3 Sodium Monomer

- Not feasible to brute force dimer with 3rd nearest neighbors
- explain nearest neighbors
- even with full 48 cubic point symmetry of the host of the defect which no structure can exceed ...
- explain confirmation of algorithm with brute force for mono sodium
- explain how plot is created with sweeps
- more complicated symmetries
- compare figures
- calculation for dimer
- discuss noteworthy structure (e.g. inner shell carved out)
- citation of paper that has the same plot Now first by brute force search we know the minima for a single sodium atom.

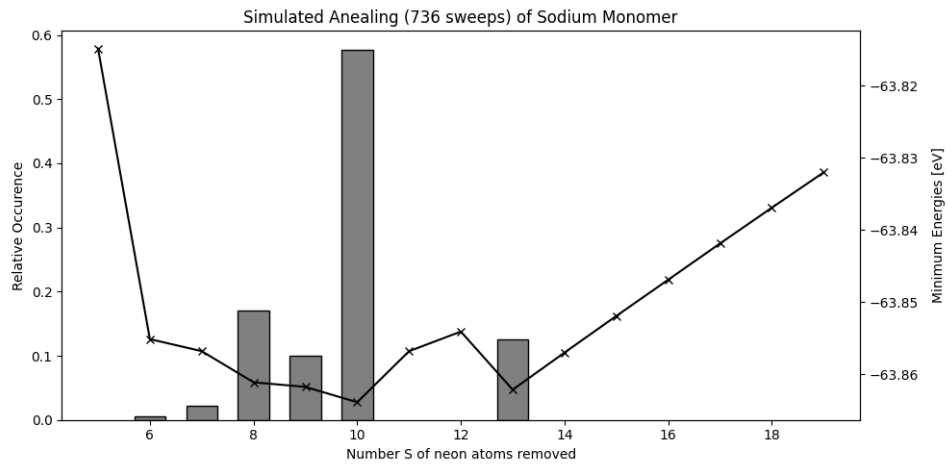


Figure 4.3: Simulated Annealing for single sodium atom inserted, compared to a brute force minima search for a fixed number of removed atoms S.

So 4.3 shows the simulated annealing algorithm accurately icks up on the location of the minima, albeit with no quantitative measure misleading local minima being blown out of proportion (See S=8).

4.4 Sodium Dimer

- in setup exxplain that dimer binding position is roughly first nearest neighbour of ne lattice -3rd nearest neighbors, why ? because minima is more the 2 shells -rough estimate of time used by brute forcing
- even with full cubic symmetry this is too long (divide b 64)
- maybe think about symmetry
- same graphics as for the monomer case
- heuristically take the maxima of these plots
- give structures
- discuss structures (inner shell carved out)

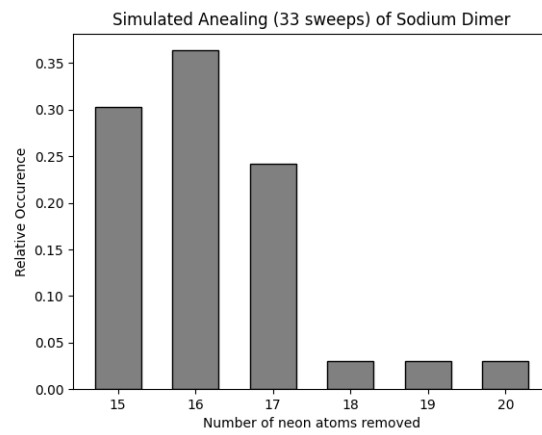


Figure 4.4: Simulated annealing results and their relative occurrence after 33 sweeps

5 DFT optical spectra results

Zweites Kapitel

6 Conclusion

Unfortunately no confidence or error can be estimated since the approach was purely heuristical. Optical spectrum does not depend much on replacements and precise structure.

7 Ausblick


Ausblick

Bibliography

- [1] P. Bitzek et al. “Structural Relaxation Made Simple”. In: *Physical Review Letters* 97.17 (2006), p. 170201. DOI: [10.1103/PhysRevLett.97.170201](https://doi.org/10.1103/PhysRevLett.97.170201).
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A Anhang

A.1 Inhalt des beigefügten Datenträgers

 Datenträger



A



a



b



c



B



a



b



A

Eidesstattliche Erklärung

Ich, Gabriel Sommer, versichere hiermit, dass ich die vorliegende Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe, wobei ich alle wörtlichen und sinngemäßen Zitate als solche gekennzeichnet habe.

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Vienna, den August 10, 2025

GABRIEL SOMMER

Declaration of Authorship

I, Gabriel Sommer, hereby declare that I have written the present thesis independently and have used no sources or aids other than those explicitly stated. All direct quotations and all paraphrased ideas have been clearly marked as such.

This work has not been submitted, either in the same or a substantially similar form, to any other examination board, nor has it been published elsewhere.

Vienna, August 10, 2025

GABRIEL SOMMER