A Quantum Chemical Approach to Cohesive Properties of NiO

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We apply ab-initio quantum chemical methods to calculate correlation effects on cohesive properties of NiO, thereby extending a recently proposed scheme to transition metal oxides with partially filled d-bands. We obtain good agreement with experiment for the cohesive energy and show that the deviation of the lattice constant at the Hartree-Fock level is mainly due to van der Waals-like interactions. Correlations enhance the stability of the magnetic ground state found at the Hartree-Fock level.

I. INTRODUCTION

NiO has a long tradition in solid-state physics as a prototype of an insulator with partially filled d-bands. The initial explanation for its unusual behavior was given by Mott [1] who argued that the Coulomb repulsion of the electrons in singly occupied nickel orbitals should completely suppress excitations of the $d \to d$ type. This picture led to the notion of Mott insulators and was later refined by Zaanen et al [2] who characterized NiO as a charge-transfer insulator with a valence band of oxygen $p$-type and a resulting $p \to d$ gap. The band structure and especially the gap have been in the center of interest and a considerable amount of work has been devoted to their determination [3,4] (for reviews on NiO see, e.g., Refs. [6], [7] and, more general, Ref. [8]). Surprisingly, only little work has been done on cohesive properties and we are aware of only one result from density functional theory (DFT). At the Hartree-Fock (HF) level, a very careful and extensive investigation has been performed [9]. In the present paper, we want to address the question how electron correlations affect ground-state properties.

In the field of atoms and molecules, the most accurate methods are those of quantum chemistry whereas in solid-state physics the dominant method is DFT. However, it has been demonstrated by using local operators combined with an incremental method that high-quality results can be obtained from a quantum-chemical approach to semiconductors [10] and ionic compounds [11]. Transition metals are still a challenge in quantum chemistry and even for the NiO molecule extensive calculations are necessary to obtain agreement with experiment.

We want to show, however, that an accurate determination of correlation effects is possible nowadays, using the afore-mentioned incremental scheme, even for solids containing transition-metal compounds. In addition, we want to compare some relevant atomic and molecular results from ab-initio quantum chemistry to those of DFT. For this purpose, we performed test calculations with the local density approximation (LDA) as well as with the gradient-corrected functional of Becke [12], Lee, Yang and Parr (BLYP) [13].

II. THE METHOD

A. Incremental scheme

The incremental scheme uses the fact that electron correlations are a local property. The first step is to calculate the correlation energy $\epsilon(AB)$ of groups of localized orbitals (the so-called one-body increments). The correlation energy of two groups of orbitals $\epsilon(AB)$ can then be expressed as

$$\epsilon(AB) = \epsilon(A) + \epsilon(B) + \Delta\epsilon(AB),$$

the non-additive part $\Delta\epsilon(AB)$ being the two-body increment. For three groups of orbitals one obtains

$$\epsilon(ABC) = \epsilon(A) + \epsilon(B) + \epsilon(C) + \Delta\epsilon(AB) + \Delta\epsilon(BC) + \Delta\epsilon(CA) + \Delta\epsilon(ABC).$$

Obviously, this series can be extended to any order of increments and for the correlation energy of the solid one obtains

$$\epsilon_{\text{bulk}} = \sum_A \epsilon(A) + \frac{1}{2} \sum_{A,B} \Delta\epsilon(AB) + \frac{1}{3!} \sum_{A,B,C} \Delta\epsilon(ABC) + ...$$

(1)

which is still exact. The approximation consists in neglecting higher than third orders of increments which makes it necessary that the sum of these increments should be negligibly small. Moreover, it is assumed that the increments rapidly decrease with increasing distance between groups $A$ and $B$. Since the calculations are performed on embedded clusters, the increments should only weakly depend on the chosen cluster. The validity of these assumptions has to be checked, of course, for each specific case. A prerequisite is that the correlation method must be size-extensive. Since the method must be applicable to all types of wavefunctions (including low-spin), we chose the quasidegenerate variational
perturbation theory (QDVPT). In the simplest case of a single-reference wavefunction, the correlation energy is obtained from the functional

$$F[\Psi_c] = \frac{\langle \Psi_{SCF} + \Psi_c | H - E_{SCF} | \Psi_{SCF} + \Psi_c \rangle}{\langle \Psi_{SCF} | \Psi_{SCF} \rangle}$$

where $\Psi_{SCF}$ is the self-consistent field wavefunction and $\Psi_c$ the correlation part obtained by single and double substitutions from the SCF determinant, i.e.,

$$|\Psi_c\rangle = \sum^c_r c^r_a a^+_r a|\Psi_{SCF}\rangle + \sum_{c<s}^c c^r_{ab} a^+_r a^+_s a|\Psi_{SCF}\rangle.$$  

The method is closely related to the coupled electron pair approximation (CEPA) and the averaged coupled-pair functional (ACPF), see the discussion in Ref. [27]. The largest increments were compared with those obtained from the coupled-cluster approach with single and double substitutions (CCSD) where an exponential ansatz for the correlated wavefunction is made:

$$|\Psi_{CCSD}\rangle = \exp(\sum^c_r c^r_a a^+_r a + \sum_{c<s}^c c^r_{ab} a^+_r a^+_s a|\Psi_{SCF}\rangle.$$  

These increments were also calculated with CCSD(T) where three particle excitations are included by means of perturbation theory. All the calculations were done with the ab-initio program package MOLPRO [28-31].

**B. Pseudopotentials and basis sets**

The calculations are performed on clusters of two or three ions which are accurately treated by quantum-chemical methods, embedded in surroundings treated at a lower level of approximation. To model the Pauli repulsion of the surroundings on the clusters considered, a pseudopotential for Ni$^{2+}$ was employed simulating a fixed [Ar] 3$d^8$ configuration, cf. Table I. The parameters have been adjusted to averaged valence energies of 12 configurations of Ni and Ni$^+$. The valence energies were taken from relativistic HF calculations using the Wood-Boring Hamiltonian [32]. The clusters were modeled in the same way as described in previous work on MgO and CaO [33]. Cluster O$^{2-}$ ions were surrounded by Ni$^{2+}$ pseudopotentials as next neighbors. The whole system was embedded in a set of point charges (typically 7 x 7 x 7 lattice sites with charges ±2 in the interior and reduced by factors of 2, 4 and 8 at the surface planes, edges and corners, respectively). The description of the ions contained within the clusters is as follows. The oxygen basis set was a [5s4p3d2f]-basis. For the nickel ions a pseudopotential with a Ne core was together with an optimized basis set described in Ref. [34] was used. The d-contraction was slightly relaxed (the three smallest exponents were used uncontracted) and three f-exponents (0.67, 2.4, 7.8) were added yielding a [6s5p4d3f] basis set. The correlated orbitals are 2$s$ and 2$p$ for O, O$^{2-}$ and the 3$d$-orbitals in the case of Ni$^{2+}$. The doubly occupied orbitals were kept closed in the reference wavefunction which leads to a single reference calculation except for the case of low-spin coupling. The cohesive energy was calculated with respect to the Ni 3$d^8$4$s^2$ state (of course, the 4$s$ orbital was correlated in that case, too). The influence of the correlation of the 3$s$ and 3$p$ orbitals of Ni will be discussed separately.

**C. Test calculations**

1. **Nickel ionization potential**

Results of test calculations for the first and second ionization potential of Ni are shown in Table II. We performed calculations with a finite basis set (indicated as ‘our basis set’) as well as, when possible, using numerical schemes which are comparable to a complete basis set (indicated as ‘finite differences’). Comparing Hartree-Fock and Dirac-Fock calculations, one finds that relativistic effects make a significant difference. The origin and importance of these effects on the results for the crystal binding energy will be discussed later. The HF calculation with the Ne-core pseudopotential and the [6s5p4d3f] basis set is in nice agreement with the Dirac-Fock result which shows that the pseudopotential is well suited to account for relativistic corrections. At the correlated level, we find that we recover most of the missing energy. Correlation of Ni 3$s$ and 3$p$ orbitals slightly improves the result; the remaining error is mostly due to basis-set deficiencies. The density functional results tend towards an overestimation.

2. **Electron affinity of oxygen**

The next test concerns the electron affinity of the oxygen atom. We find a value of 1.359 eV at the QDVPT level (exp.: 1.461 eV [35]). Note that with several density functionals negatively charged ions are not stable because of the wrong asymptotic behavior of the functionals (see the discussions in Ref. [36, 37]). Indeed, we found positive orbital energies when applying LDA and BLYP to the O$^-$ ion which indicates the instability.

3. **Ground state of the NiO molecule**

A final test calculation was performed for the $^3\Sigma^-$ ground state of the NiO molecule (see Table II). Our multi-reference averaged coupled-pair functional (MR-ACPF) result for D$_i$ is in good agreement with the experimental result. The bond length is slightly too short and therefore the vibrational frequency is too high (calculating the vibrational frequency at the experimental
bond length gives a value of 897 cm\(^{-1}\) which is in better agreement with experiment. Enlarging the basis sets by using \(g\) functions leads to a further slight reduction of the bond length. Correlating the Ni 3p orbitals also reduces the bond length (by \(\sim 0.005\) Å). Therefore, an enlargement of the active space (the group of orbitals from which the reference determinants of the MR-ACPF calculation are formed) seems to be necessary. The lowest-lying virtual orbitals not yet included in the active space are of \(\pi_x\) and \(\pi_y\) type. However, inclusion of these orbitals is not feasible currently due to the high computational effort. Bauschlicher[8] added another virtual \(\sigma\) orbital to the active space, but on the other hand the \(\delta\) orbitals and the O 2s-orbital were kept closed (i.e. correlated, but doubly occupied in the reference wavefunction). This gave excellent agreement with experiment. However, it is obvious from his work that the results are still sensitive to the correlation level applied (see the comparison in Ref. [8]). Actually, we found that this problem is more critical in the case of the molecule than in the calculations performed for the solid (QDVPT calculations, e.g., are difficult to converge for the molecule). Note that, in contrast to the solid, the NiO molecule is covalently bonded with charges \(\pm 0.7\) according to a Mulliken population analysis. The gradient-corrected DFT results for NiO are excellent for the vibrational frequency and the bond analysis. The gradient-corrected DFT results for NiO with charges \(\pm 0.7\) according to a Mulliken population (\(\pi\) orbitals in the reference wavefunction). This gave excellent agreement with experiment. However, it is obvious from his work that the results are still sensitive to the correlation level applied (see the comparison in Ref. [8]). Actually, we found that this problem is more critical in the case of the molecule than in the calculations performed for the solid (QDVPT calculations, e.g., are difficult to converge for the molecule). Note that, in contrast to the solid, the NiO molecule is covalently bonded with charges \(\pm 0.7\) according to a Mulliken population analysis. The gradient-corrected DFT results for NiO are excellent for the vibrational frequency and the bond length, but for the dissociation energy one finds a significant overbinding. This might change with improved functionals such as B3LYP or B3PW91 which are not yet implemented in MOLPRO.

III. RESULTS FOR THE SOLID

A. Incremental expansion and magnetic properties

Regarding the one-body correlation energy increments (see Table IV), one finds nearly the same value for the increment \(O \rightarrow O^{2-}\) as in the systems MgO and CaO whereas the increment \(Ni \rightarrow Ni^{2+}\) is significantly larger than the corresponding value in the case of the alkaline earth oxides[6]. As compared to Mg, the low lying \(d\)-orbitals led to an enhanced core-valence correlation and a larger increment for Ca \(\rightarrow Ca^{2+}\). The near-degeneracy effects in the Ni atom lead to an even higher valence correlation energy. The two-body increments between two oxygen ions are nearly 50% larger than those of MgO although the lattice constants are very similar. This may be connected with an increased polarizability of \(O^{2-}\) in NiO which in turn might be related to the availability of low-lying open-shell \(d\)-orbitals in \(Ni^{2+}\).

As in the systems MgO and CaO, the Mulliken population analysis gives an \(X \rightarrow O\) charge transfer of slightly less than 2. The Ni-O two-body increments turn out to make the most significant correlation contribution. This is not surprising since the polarizability of the open-shell Ni\(^{2+}\) ion is roughly six times higher than that of Mg\(^{2+}\). We used a special procedure to evaluate the Ni-O increments for technical reasons. Single external correlation contributions to \(\epsilon (O^{2-})\) involving single substitutions from localized \(O^{2-}\) \(2s\), \(2p\) orbitals into unoccupied orbitals, were not directly calculated for the embedded \(Ni^{2+} \ O^{2-}\) cluster but were transferred from a calculation for a single \(O^{2-}\) embedded in large-core Ni\(^{2+}\) pseudopotentials.

Analyzing the correlated wavefunction in the case of the Ni-O increments for next neighbors, one finds that internal excitations (excitations from the oxygen ion to the singly occupied nickel orbitals) are negligibly small and contribute with a few \(\mu H\) (Hartree units, 1 \(\mu H=27.2114\) eV) only. This is certainly a consequence of the large Coulomb repulsion \(U\) in the case of doubly occupied Ni 3\(d\)-orbitals. Another interesting feature is the importance of spin-flips on the Ni site. By restricting the excitations for the supersystem, the Ni\(^{2+}\) and O\(^{2-}\) ions to double externals (only two-particle excitations to completely unoccupied orbitals are allowed, excitations to orbitals already occupied with an electron of opposite spin are forbidden), one obtains an increment of only 0.008450 \(\times 6H\) instead of 0.011534 \(\times 6H\) when single external excitations are additionally taken into account. Thus, the importance of single externals becomes obvious. The processes among the single externals which are the most important ones for the increment are those where an electron from the \(O^{2-}\) ion is excited to a singly occupied Ni orbital and the Ni electron is excited to a virtual orbital which results in an effective spin-flip (Fig. 1). Of course these processes are only possible in open shell systems. In the case of the oxygen-oxygen increment for next neighbors, neglect of single externals only slightly reduces the increment from 0.003916 \(\times 6H\) to 0.003549 \(\times 6H\). This confirms that single externals have their main impact on increments involving open shells.

The Ni\(^{2+}\)-Ni\(^{2+}\) increments were calculated for the case of high \((S=2)\) and low spin \((S=0)\) coupling (neglecting single externals). However, the very small energy splitting between the states is sensitive to the chosen cluster and increases when point charges as next neighbors are replaced by explicitly treated oxygens. Therefore, the results in Table IV should not be used for a quantitative evaluation of the splitting. In the case of a cluster of the type \((O(0,0,0)-Ni(0,0,1)-Ni(0,0,-1))\), the splitting is 138 \(\mu H\) at the HF level and 276 \(\mu H\) at the correlated level including single external excitations (the \(S=0\) state is lower). For next neighbors, one finds a tendency towards ferromagnetic coupling: in the cluster \((O(0,0,0)-Ni(0,0,1)-Ni(0,1,0))\), the \(S=2\) state is 19 \(\mu H\) lower at the HF level and 22 \(\mu H\) when correlations are included. These results are in qualitative agreement with experiment where the exchange coupling is ferromagnetic for next neighbors and antiferromagnetic for second next neighbors[6]. This indicates that the stability of the antiferromagnetic AF\(_2\) state (a state with parallel spins in (1 1 1) planes, adjacent planes having antiparallel spin) found at the HF level, will be enhanced due to corre-
lations. Although quantitative values for the exchange coupling could be calculated for molecules and are in agreement with experiment (see, e.g., Ref. 11), the situation is more difficult in solids and the exchange coupling increases with the number of ions explicitly treated. Therefore, our results can only give a qualitative picture here. Note that the order of magnitude of the magnetic splitting (0.03 eV/double cell at the HF level) is much smaller than the total cohesive energy.

The incremental expansion for the correlation contribution to the cohesive energy is well convergent. The two-body increments show a rapid van der Waals like decrease and the sum of the three-body corrections is small compared to the sum of one- and two-body increments. It is interesting to see that the two-body increments amount to roughly 80% of the correlation contribution to the cohesive energy, while the intra-ionic contributions contained in the one-body increments yield only ∼20% (in the case of the alkaline earth systems, both contributions were roughly of the same size). The QD-VPT results are closer to CCSD(T) than to CCSD, but the results are weakly dependent only on the method applied. Individual increments and their total contribution to the bulk cohesive energy for a lattice spacing of 4.17 Å are displayed in Table VII and Figure 2.

### B. Comparison with experiment

Our reference value for the HF binding energy (6.2 eV) is taken from Ref. 14. However, two corrections are necessary: since the calculations of Ref. 14 were done within the unrestricted Hartree-Fock (UHF) approximation for the solid, but the restricted Hartree-Fock (RHF) level for the atoms, a part of the correlation energy is already included in that value. We corrected this by subtracting the energy difference \(|E_{UHF} - E_{RHF}|\) for the Ni\(^{2+}\) ion (-0.0072 H) from the binding energy of Ref. 14. This correction can be viewed as a ‘one-body correction’ which is tantamount to applying Eq. [1] not to the correlation energy but to the difference UHF-RHF. Since the correction is nearly the same for the case of a system with a Ni\(^{2+}\) and an O\(^{2-}\) ion, we conclude that the two-body corrections are negligible and the HF cohesive energy of Ref. 14 should be reduced by 0.007 H. A second correction is necessary, since the CRystalAL calculation was done neglecting effects arising from relativistic effects. These effects gain importance beginning with the first row of transition metals. We found (see Table I) that the first and second ionization potentials of Ni increase from 0.840 H (Hartree-Fock calculation) to 0.853 H (Dirac-Fock calculation). This is a consequence of the relativistic contraction (and stabilization) of the Ni 4s-orbital. In the case of Ca, this correction is of the order of 2.4 mH only. Spin-orbit effects are negligible for Ni as the d-occupation in the solid is \(d^8\) (\(6p^2\),\(5d^2\)) and very similar to that of the isolated atom (\(3P\)). Taking both corrections into account, we obtain a cohesive energy of 5.65 eV (5.59 eV at 4.17 Å, using the bulk modulus from Ref. 4). Adding the zero-point vibrations (0.12 eV, a Debye approximation with \(\Theta \approx 640K\) was used) to the experimentally determined cohesive energy of 9.5 eV, we thus deduce an ‘experimental’ correlation contribution to the cohesive energy of \(\approx 4.0\) eV. Within the basis sets used, we recover 3.38 eV (\(\approx 84\%\)) of this energy with our local correlation scheme.

### C. Lattice constant

By performing the incremental expansion for a second value of the lattice constant \(a\), we obtain the correlation correction to \(a\). The same physical picture as in the case of MgO and CaO is found: the van der Waals like interaction between the ions (included in the two-body increments) reduces the lattice constant whereas correlations in the oxygen ion tend to enhance the lattice constant. The latter effect is due to the lower level spacing and therefore increasing importance of correlations at larger lattice constant. The results for \(a=4.264\) Å are displayed in Table VIII. Concerning the three-body increments, we used the two largest ones to evaluate the lattice constant. By linearly fitting the correlation energy and using the bulk modulus from the CRYSTAL calculation (214 GPa), we obtain a value of 4.167 Å, i.e., a reduction by 0.097 Å with respect to the CRYSTAL-HF result. This is in nice agreement with the experimental result of 4.17 Å. We assumed a NaCl structure and did not take into account the slight rhombohedral distortion observed in the experiment. The calculated cohesive energy at this equilibrium constant is (5.65-0.06+3.38) eV=8.97 eV which is 93 % of the total cohesive energy of 9.6 eV.

Finally, we evaluated the one-body and two-body Ni-O increments when electrons in the Ni 3s and 3p orbitals are correlated. At a lattice constant of 4.17 Å, we find that the one-body increment Ni → Ni\(^{2+}\) increases from 0.074545 to 0.080790 as a consequence of the outer-core-valence correlation. On the other hand, the absolute value of the sum of the Ni-O increments increases from 0.073446 to 0.082706. As these effects have the opposite sign, they nearly cancel and increase the correlation contribution to the cohesive energy to 0.127204 H at 4.17 Å. The lattice constant is reduced to 4.151 Å.

### D. Comparison with results from literature

Our results for the cohesive energy are in better agreement with experiment than those of DFT, where a significant overestimation was found. The lattice constant of the latter work (4.183 Å) is in good agreement with experiment. A recently performed Quantum Monte-Carlo (QMC) calculation gives good agreement with experiment, but the error-bars are quite large compared to
those of other QMC work. Moreover, the basis sets are very small and not adjusted to the pseudopotential used.

**IV. CONCLUSION**

In conclusion, we have shown that the incremental scheme is capable of accurately treating systems with open $d$-shells. We obtained more than 84% of the correlation contribution to the cohesive energy or 93% of the total cohesive energy. Contributions from interatomic origin are roughly four times larger than those due to the formation of ions. The lattice constant agrees well with experiment. The stability of the magnetic ground state obtained found at the HF level is enhanced with the inclusion of correlations. We feel that the quality of this calculation is superior to previous work with DFT and QMC.

**ACKNOWLEDGMENTS**

We are grateful to Prof. H.-J. Werner (Stuttgart) for providing the program package MOLPRO and to Dr. N. M. Harrison (Daresbury) for useful information on the CRYSTAL calculations.

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FIG. 1. Spin ordering: a) in the ground state of NiO; b) for a double external configuration with simultaneous excitations from a Ni$^{2+}$ and an O$^{2-}$ ion; c) for a single external configuration with spin-flip.

FIG. 2. Result of the incremental expansion for NiO at a lattice constant of 4.17 Å.
Parameters of the Ni\(^{2+}\) pseudopotential. The pseudopotential has the form 
\[ V(r) = -\frac{Q}{r} + \sum_j \sum_k A_{jkl} \exp(-a_{jkl}r^2) \sum_m |lm_i><lm_i| \].

| Q | l | k | A\(_{jkl}\) | a\(_{jkl}\) |
|---|---|---|-----------|-----------|
| 2 | 0 | 1 | 6.3098777 | 0.8926553 |
|   | 0 | 2 | -0.7025295 | 0.3059013 |
| 1 | 1 | 1 | 3.2304525 | 0.7566913 |
|   | 2 | 2 | -0.2278919 | 0.2415367 |
| 2 | 1 | 1 | 1.1107680 | 0.3984276 |
|   | 3 | 1 | -0.5915083 | 0.4892060 |

Table II. Sum of first and second ionization potentials for Ni in Hartree units (\(^3\)F state)

| Method | \(\text{Ni} \rightarrow \text{Ni}^{2+}\) | \(\text{O} \rightarrow \text{O}^{2+}\) | \(\text{sum of one-body increments}\) | \(\text{sum of Ni-O increments}\) | \(\text{sum of Ni-Ni increments}\) | \(\text{sum of two largest three-body increments}\) | \(\text{total sum}\) |
|--------|-----------------|---------------|------------------|------------------|------------------|-----------------|-----------------|
| Hartree-Fock, finite differences | 0.840310 | -0.026278 | -0.026278 | -0.001686 | -0.000192 | +0.003572 | -0.124189 |
| Dirac-Fock, finite differences | 0.852950 | -0.069204 | -0.069204 | -0.007850 | -0.000942 | +0.002724 | -0.147709 |
| Hartree-Fock with relativistic pseudopotential, our basis | 0.855544 | -0.009578 | -0.009578 | -0.000042 | -0.000192 | +0.001922 | -0.131489 |
| QDVPT (3d, 4s correlated), our basis | 0.930863 | -0.100823 | -0.100823 | -0.000025 | -0.000192 | +0.002724 | -0.147709 |
| QDVPT (3s, 3p, 3d, 4s correlated), our basis | 0.936216 | -0.095787 | -0.095787 | -0.000025 | -0.000192 | +0.002724 | -0.147709 |
| LDA, our basis | 0.999031 | -0.000042 | -0.000042 | -0.000042 | -0.000192 | +0.002724 | -0.147709 |
| BLYP, our basis | 0.982560 | -0.000019 | -0.000019 | -0.000019 | -0.000192 | +0.002724 | -0.147709 |
| expt. | 0.947760 | -0.000019 | -0.000019 | -0.000019 | -0.000192 | +0.002724 | -0.147709 |

Table III. Bond length \(R_e\) (Å), dissociation energy \(D_e\) (eV) and vibrational frequency \(\omega_e\) (cm\(^{-1}\)) of the NiO molecule. The orbitals correlated with the multi-reference averaged coupled-pair functional (MR-ACPF) scheme are O 2s, 2p, Ni 3d, 4s. The dissociation energy is calculated with respect to the \(^3\)D \((d^9s^1)\) state of Ni. The DFT calculations for the atoms were performed without applying a spherical approximation for the potential and with integer occupation numbers.

| Method | \(R_e\) | \(D_e\) | \(\omega_e\) |
|--------|-------|-------|-------|
| MR-ACPF | 1.601 | 3.62 | 958 |
| LDA | 1.584 | 6.12 | 932 |
| BLYP | 1.626 | 4.73 | 861 |
| Ref. | 1.626 | 3.80 | 859 |
| expt. | 1.627 | 3.92±0.03 | 858 |

Table IV. Local correlation energy increments (in H) at a lattice constant of 4.17 Å, from QDVPT calculations. The largest increments are compared with CCSD and CCSD(T). The numbers in brackets (a,b,c) are indices of the lattice site of the ion and are given in multiples of the lattice constant. \(S\) denotes the spin coupling \((S = 2\text{ means ferromagnetic, } S = 0\text{ antiferromagnetic coupling})\). The increments are already multiplied with the weight factor except where the weight factor is explicitly repeated in the sum. A weight factor of 0 means that this state does not occur in the AF\(_2\) state. In the case of the three-body increments, we summed only over the two largest ones in order to make a comparison with the results of Table V possible.

| Weight | QDVPT | CCSD: | CCSD(T): | sum of one-body increments | sum of Ni-O increments | sum of Ni-Ni increments | sum of two largest three-body increments | total sum |
|--------|--------|--------|--------|--------------------------|-----------------------|------------------------|-----------------------------|----------|
| 1 | +0.074545 | +0.068628 | +0.073366 | -0.026278 | -0.073446 | -0.001686 | +0.003572 | -0.124189 |
| 1 | -0.100823 | -0.099578 | -0.105364 | -0.026278 | -0.073446 | -0.001686 | +0.003572 | -0.124189 |
TABLE V. Local increments (in H) for NiO at a lattice constant of 4.264 Å.

| Increment Type                        | Value      |
|---------------------------------------|------------|
| sum of one-body increments            | -0.028014  |
| sum of Ni-O increments                | -0.068362  |
| sum of Ni-Ni increments               | -0.001416  |
| sum of O-O increments                 | -0.025207  |
| sum of three-body increments          | +0.003088  |
| total sum                             | -0.119911  |
\[
\begin{array}{ccccccc}
O & 2s, 2p & \text{Ni} & d_{xy} & d_{xz} & d_{yz} & d_{z^2} & d_{x^2-y^2} & \text{virtual} \\
\end{array}
\]

a) 
\[
\begin{array}{ccccccc}
\uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow & \uparrow \\
\end{array}
\]

b) 
\[
\begin{array}{ccccccc}
\uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \uparrow & \\
\end{array}
\]

c) 
\[
\begin{array}{ccccccc}
\uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow & \\
\end{array}
\]
Incremental expansion for NiO

- one-body increments
- two-body increments
- three-body increments
- sum of increments
- exp. value