

Nuclear Quadrupole Interactions in Cadmium Complexes: Semiempirical and *ab initio* Calculations

Lars Hemmingsen^{a,b}, Ulf Ryde^a, and Rogert Bauer^b

^a Department of Theoretical Chemistry, Chemical Centre, University of Lund,
P. O. Box 124, S-221 00 Lund, Sweden

^b Department of Mathematics and Physics, The Royal Veterinary and Agricultural University,
Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

Reprint requests to Dr. L. H.; Fax: +45 35282350; E-mail: lhe@kvl.dk

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Semiempirical calculations, based on the so-called angular overlap model, have been compared with *ab initio* methods (MP2) for the calculation of nuclear quadrupole interactions (NQI's) in cadmium complexes with biologically relevant ligands (H₂O, OH[−], cysteinate, carboxylate, and imidazole). The assumptions on which the semiempirical model is based have been tested and the comparison indicates that: 1) A change in the Cd–ligand bond length by 0.1 Å may change the electric field gradient (EFG) by about 0.2 a. u.. A simple scheme to incorporate such effects in the semiempirical method is suggested. 2) The effect of ligand–ligand interactions is up to about 0.2 a. u. for the largest diagonal element of the EFG tensor for the tested complexes, and such effects can significantly influence the so-called asymmetry parameter. 3) The position of non-coordinating atoms on the ligands can in some cases (e. g. the hydrogen atoms of water) significantly influence the EFG. The combined effect of non-coordinating atoms and ligand–ligand interactions may cause deviations of up to 0.35 a. u. between *ab initio* and the semiempirical calculations. 4) In the semiempirical model each ligand is characterised by one parameter, the so-called partial nuclear quadrupole interaction. This parameter has been evaluated by *ab initio* calculations, and agreement was found within about 0.2 a. u. (≈ 40 Mrad/s) for all ligands except imidazole. 5) A change in the coordination number from 2 to 6 may change the partial NQI by about 0.3 a. u.

Key words: Electric Field Gradient; Angular Overlap Model; Ligand Additivity.

1. Introduction

Nuclear quadrupole interactions (NQIs) in cadmium complexes have been investigated in several experimental studies using the technique of perturbed angular correlation of γ -rays (PAC) [1]. The elements of the electric field gradient (EFG) tensor at the cadmium nucleus can be derived from the experiments, provided that the nuclear quadrupole moment, Q , is known. For ^{111m}Cd, the relation is

$$\omega_{ab} = \frac{3}{20\hbar} |eQV_{ab}|, \quad (1)$$

where ω_{ab} are the elements of the NQI tensor (a and b are cartesian coordinates), e is the elementary charge, V_{ab} are the elements of the EFG tensor, and \hbar is Planck's constant divided by 2π .

Calculations of EFGs in cadmium complexes have been performed with *ab initio* or density functional methods [2 - 9] as well as more approximate methods [10 - 12]. In particular, the semiempirical model of Bauer et al. [11] has been successfully applied for the calculation of NQIs for complexes with metal ligands typically found in biological systems (e. g. H₂O, imidazole, Cl[−], thiolate, thioether, carboxylate, and carbonyl groups). This method is a modified version of the so-called angular overlap model [13], which has been useful in describing absorption spectra of transition-metal complexes. In the following, this modified angular overlap model designed for NQI calculations in cadmium complexes will be denoted the AOM.

The underlying idea of the AOM is that the EFG at the cadmium nucleus is produced by the partial filling

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of 5p orbitals on cadmium and by the charge on the ligands (if any). This may be considered as a bonding and an ionic contribution to the EFG, respectively. The AOM is based on three assumptions:

- The ligands are independent, i.e. they do not interact.
- The NQI produced by a ligand is axially symmetric. This means that σ , but not π , bonds are included. However, the model has the potential to include π -bonding as well.
- The NQI produced by a ligand is independent of the Cd–ligand bond length (within reasonable limits).

Under these assumptions, each ligand is completely characterised by one parameter, the so-called partial NQI, ω_l (l for ligand). The total NQI tensor in a complex is the sum of the NQIs from each ligand (in a coordinate system with the cadmium nucleus at the origin):

$$\omega_{ab} = \sum_{l=1}^N \omega_l \left(\frac{3}{2} \alpha_l \beta_l - \delta_{a,b} \right), \quad (2)$$

where α_l and β_l are the directional cosines to the l th ligand (for $a = x, y, z$, $\alpha_l = \cos(\phi_l) \sin(\theta_l)$, $\sin(\phi_l) \sin(\theta_l)$, $\cos(\theta_l)$, respectively, where θ_l and ϕ_l are the polar and azimuthal angle of the ligand, and correspondingly for b and β_l), $\delta_{a,b}$ is the Kronecker delta, and ω_l is the partial NQI for the l th ligand. Partial NQIs for several ligands have been determined experimentally from PAC measurements on model complexes [11, 14, 15]. A more detailed description of the AOM can be found in [11].

In this paper, *ab initio* calculations of EFGs in cadmium complexes are used to test AOM calculations. The following investigations have been performed:

- Partial NQIs calculated by *ab initio* methods have been compared to those used in the AOM.
- The coordination number has been varied from two to five in complexes with only one type of ligand, as a test of the assumption of independent ligands.
- Two-, four-, and six-coordinate complexes with two different ligands have been studied to evaluate how much ligand–ligand interactions influence the EFG. This also tests the assumption of independent ligands.
- The effect of changing the Cd–ligand bond lengths has been investigated.

2. Methods

2.1. Structures

The two-, three-, four-, five-, and six-coordinate complexes were linear, trigonal, square planar or tetrahedral, square pyramidal, and octahedral, respectively. The Cd–Cl, Cd–N, Cd–S, Cd–O (monodentate carboxylate), Cd–OH₂, and Cd–OH[−] bond lengths were 2.51, 2.26, 2.61, 2.39, 2.35, and 2.15 Å, respectively, unless otherwise stated. These distances are the averages of the bond lengths found in the model complexes constituting the experimental basis of the AOM. The thiolate group is a bridging ligand in the model complexes; therefore this bond length may be slightly longer than in non-bridging cases. OH[−] is not present in any of the model complexes, and a bond length 0.2 Å shorter than the one for water was used. The geometries of H₂O and imidazole were taken from [16, 17], and those of cysteine, aspartate, histidine, and OH[−] were taken from the fragment library in the program InsightII version 2.3.0 [18]. The geometries of CH₃S[−] and CH₃COO[−] were created by truncating the corresponding amino acids and saturating the broken bond with a hydrogen atom. For cysteinate, aspartate, and histidine the cadmium ion was positioned by replacing the appropriate hydrogen atom (of the corresponding neutral or positively charged amino acids) and elongating the bond. Amino acids with neutral termini were used, i.e. not the zwitterions, in order to avoid contributions from the charges on COO[−] and NH₃⁺. For OH[−], the Cd–O–H angle was chosen to be 109.5°.

2.2. Methods and Basis Sets

The calculation of EFGs in cadmium complexes follows the procedure suggested by Hemmingsen and Ryde [3]. The EFGs were calculated at the MP2 level using the generally contracted, polarised basis set of Kellö and Sadlej [19] [19s15p11d4f/11s9p5d2f] for cadmium and the 6-31G(d) basis [20–22] for the other atoms. Only the five pure d functions and the seven pure f functions were used in the calculations. The core orbitals on all atoms (1s through 3d on cadmium) were kept frozen. An MP2 calculation on CdCl₂ showed that the elements of the EFG change by less than 0.1% if no orbitals are frozen. This procedure has been shown to reproduce experimental results to within about 0.3 a. u. at the restricted Hartree–Fock

level [3]. The calculations were carried out on IBM RISC RS/6000, Cray C90, Silicon Graphics Origin 200 MIPS R10000, and DEC alpha 200 4/166 workstations using the program packages Gaussian94 [23] and MOLCAS 3.1 [24].

2.3. Reaction Field

For some of the chloride complexes, a reaction field was introduced (because the high coordination numbers give rise to negatively charged complexes) as described by Friedman [25]. A cavity radius of 4.51 Å was chosen (2 Å longer than the Cd–Cl bond length), and the cadmium ion was placed at the centre of the cavity. In this model, the field in the cavity is produced by a set of so-called image charges positioned appropriately around the molecule. The magnitude of the image charges was calculated from the Mulliken charges of the Cl[−] ions (obtained in a vacuum calculation). A dielectric constant of 5 was chosen, as a somewhat arbitrary guess of the effective dielectric constant, ϵ , near the cadmium ion in the crystals of the model complexes constituting the basis for the AOM. The results are not sensitive to this choice when ϵ is larger than about 3, and the aim of these calculations was to estimate the effect from the surrounding crystal, rather than to perform a quantitative determination.

2.4. Coordinate Systems in which EFGs are Presented

The EFGs presented in Tables 1, 3–5 are calculated in the coordinate systems that diagonalise the NQI tensor calculated using the AOM, with $|\omega_{zz}| \geq |\omega_{yy}| \geq |\omega_{xx}|$.

It is important to note that these coordinate systems do not always coincide with the principal axis system of the EFG (determined by *ab initio* calculations). However, if one wants to make comparisons with other calculations of EFGs (or NQIs), for example *ab initio* calculations as in this work, it is essential to use the same coordinate system. It is noted in the table captions when an off-diagonal element with significant magnitude is present in the *ab initio* calculations. In all *ab initio* calculations, the EFG tensor is reported as the numerically largest diagonal element V_{zz} and the so-called asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. η is zero in an axially symmetric complex (i. e. in terms of EFGs, the x and y directions are equivalent) and always between zero and unity in magnitude.

Table 1. Comparison of partial NQIs, ω_I , from *ab initio* calculations and from the AOM. All structures have at least C_i symmetry (the coordinates are available as supplementary material). The first two columns refer to the calculated EFG. The third column is the partial NQI to be used in the AOM in order to reproduce the *ab initio* EFG, and the fourth column is the empirical partial NQI from the AOM. The partial NQIs are conventionally chosen as positive.

	η	<i>ab initio</i> V_{zz} a. u.	ω_I Mrad/s	AOM ω_I Mrad/s
CdCl ₂	0.000	−2.964	273	231
[Cd(H ₂ O) ₂] ²⁺	0.173	−2.032	187	207
Cd(CH ₃ S) ₂	0.279	−3.171	292	300
Cd(CH ₃ COO) ₂ ^{c,d}	0.075	−2.711	249	245
[CdIm ₂] ²⁺ ^a	0.147	−3.422	315	95
[CdIm ₂] ²⁺ ^b	0.073	−3.420	315	95
Cd(OH) ₂ ^d	0.176	−3.796	349	—

^a Planar structure. ^b The angle between the two imidazole rings was 45°. ^c Monodentate. ^d An off-diagonal element (not shown) is larger than 10% of $|V_{zz}|$.

2.5. Nuclear Quadrupole Moment

A nuclear quadrupole moment of 0.83 barn [26] was used for the $I = 5/2$ nuclear level of ¹¹¹Cd (values ranging from 0.73 to 0.83 barn have been reported [27]). This means that an EFG of 1 a. u. corresponds to an NQI of 184 Mrad/s.

3. Results and Discussion

3.1. Partial NQIs

Table 1 shows the EFG calculated by *ab initio* methods for a number of linear two-coordinate complexes (this geometry was used because it is representative also for higher coordination numbers, see below). This allows us to compare partial NQIs obtained with the two methods, i. e. the partial NQI used in the AOM and the partial NQI one has to use in the AOM to get the V_{zz} found in the *ab initio* calculations. The latter is simply $(\frac{1}{2}|V_{zz}| \times 184)$ Mrad/s for linear two-coordinate complexes. Six different ligands were tested and all compare reasonably well (within 15% or 42 Mrad/s), except imidazole. The partial NQI for OH[−] has not been determined experimentally. It is an important parameter because OH[−] is often assumed to be a ligand of active-site metal ions in proteins at high pH. Therefore we recommend the *ab initio* value in Table 1, $\omega_{\text{OH}^-} = 349$ Mrad/s, for the use in AOM.

Table 2. Test of a partial NQI for imidazole of 350 Mrad/s in AOM calculations. ω_{zz} is the numerically largest eigenvalue of the NQI tensor, see Eq(2). Because the sign is not measured experimentally, only absolute values are presented. In all these complexes the cadmium ion is six-coordinated. All other partial NQIs were kept at the values normally used in the AOM [11]. For references to experiments and structures see [11], from which also the nomenclature for the complexes has been adopted.

	AOM-calculation		PAC-experiment	
	η	$ \omega_{zz} $ Mrad/s	η	$ \omega_{zz} $ Mrad/s
Cd(Im) ₂ Cl ₂	0.18	238	0.13	275
Cd(Im) ₃ SO ₄ H ₂ O	0.74	191	0.85	210
CdglyglyImCl	0.98	177	0.35	131
Cd(His) ₂	0.75	415	0.35	161

For CH₃S[−], CH₃COO[−], and imidazole, the full amino acid (cysteinate, aspartate, and histidine, respectively) was also tested, but the relative change of the partial NQI was less than 2% (with histidine, this calculation was carried out at the Hartree–Fock level). Neither did we find any significant effect (less than 1%) on the EFG if p functions [21] were added to the hydrogen atoms. In the calculations on the full histidine amino acid (which had slightly different bond lengths and angles than those in the model of free imidazole) coordination of the N_δ as well as the N_ε nitrogen was tested. In these calculations the elements of the EFG differed by less than 5% from those of imidazole.

In order to test whether the large deviation for imidazole is due to π bonding, which is not treated by the current version of the AOM, we performed a calculation with an angle of 45° between the two imidazole planes. As can be seen in Table 1, this did not affect the partial NQI, and consequently this possibility is not likely. Furthermore, we performed a calculation on a deprotonated imidazolite ion, i.e. on a neutral Cd(Im)₂ complex. This caused only minor changes (less than 5%).

Another approach is to assume that the partial NQI calculated by *ab initio* methods is correct, and to see whether this value can be successfully applied in the AOM. This was done for the four model complexes constituting the basis of the AOM that contain imidazole or histidine, see Table 2. A partial NQI of 350 Mrad/s for imidazole was used, which is approximately the average of the partial NQIs for this ligand in two- to five-coordinate complexes (see Table 3). All other partial NQIs were kept at the

Table 3. Comparison of *ab initio* and AOM calculations for different coordination numbers. See the text for an explanation of V_{zz}^{norm} and $\langle V_{zz}^{\text{norm}} \rangle$.

	<i>ab initio</i>		AOM		<i>ab initio</i> /AOM	$\langle V_{zz}^{\text{norm}} \rangle$ a. u.
	η	V_{zz} a. u.	η	ω_{zz}	V_{zz}^{norm} a. u.	
CdCl ₂	0.000	−2.964	0	$2\omega_{\text{Cl}}$	1.482	1.436
[CdCl ₃] [−]	0.000	2.440	0	$-\frac{3}{2}\omega_{\text{Cl}}$	1.627	
[CdCl ₄] ^{2−}	0.000	2.869	0	$-2\omega_{\text{Cl}}$	1.435	
[CdCl ₅] ^{3−}	0.000	1.202	0	$-\omega_{\text{Cl}}$	1.202	
CdCl ₂ + reaction field	0.000	−2.662	0	$2\omega_{\text{Cl}}$	1.331	1.240
[CdCl ₃] [−] + reaction field	0.000	1.920	0	$-\frac{3}{2}\omega_{\text{Cl}}$	1.280	
[CdCl ₄] ^{2−} + reaction field	0.000	2.126	0	$-2\omega_{\text{Cl}}$	1.108	
[Cd(H ₂ O) ₂] ²⁺ a	0.173	−2.032	0	$2\omega_{\text{H}_2\text{O}}$	1.016	
[Cd(H ₂ O) ₂] ²⁺ d	0.000	−2.030	0	$2\omega_{\text{H}_2\text{O}}$	1.015	1.072
[Cd(H ₂ O) ₃] ²⁺ a	0.000	1.380	0	$-\frac{3}{2}\omega_{\text{H}_2\text{O}}$	0.920	
[Cd(H ₂ O) ₃] ²⁺ b	0.000	1.863	0	$-\frac{3}{2}\omega_{\text{H}_2\text{O}}$	1.242	
[Cd(H ₂ O) ₄] ²⁺ a	0.000	1.760	0	$-2\omega_{\text{H}_2\text{O}}$	0.880	
[Cd(H ₂ O) ₄] ²⁺ b	0.000	2.354	0	$-2\omega_{\text{H}_2\text{O}}$	1.177	1.893
[Cd(H ₂ O) ₅] ²⁺ c	0.096	1.253	0	$-\omega_{\text{H}_2\text{O}}$	1.253	
[CdIm ₂] ²⁺ a	0.147	−3.422	0	$2\omega_{\text{Im}}$	1.711	
[CdIm ₂] ²⁺ d	0.000	−3.418	0	$2\omega_{\text{Im}}$	1.709	
[CdIm ₃] ²⁺ a	0.000	2.653	0	$-\frac{3}{2}\omega_{\text{Im}}$	1.769	
[CdIm ₃] ²⁺ b	0.000	3.261	0	$-\frac{3}{2}\omega_{\text{Im}}$	2.174	
[CdIm ₄] ²⁺ b	0.000	4.052	0	$-2\omega_{\text{Im}}$	2.026	
[CdIm ₅] ²⁺ c	0.065	1.968	0	$-\omega_{\text{Im}}$	1.968	

^a All atoms in a plane. ^b Non-coordinating atoms placed such that each H₂O or imidazole ring lies in a plane perpendicular to the plane of cadmium and the coordinating atoms. ^c As ^b with an additional ligand along the axis perpendicular to the plane of cadmium and the other four coordinating atoms. ^d The planes of the two ligands are at right angles.

values normally used in the AOM. Considering that the other partial NQIs were not reoptimised, the two first complexes give good results compared to experiment, the third gives a fair agreement, but the last is completely off. Therefore we performed an *ab initio* calculation at the Hartree–Fock level on the latter complex (bis-(L-histidino)cadmium(II)dihydrate [28]). The results compare reasonably well with experiment. Calculated: $V_{xx} = 0.02$ a. u., $V_{yy} = 0.66$ a. u., $V_{zz} = -0.68$ a. u., experimental: $V_{xx} = 0.28$ a. u., $V_{yy} = 0.59$ a. u., $V_{zz} = -0.88$ a. u. (the sign is adopted from the calculation). This indicates that the *ab initio* calculations are correct (to within 0.3 a. u.) compared to experiment, and therefore that a full reoptimisation of the other partial NQIs might allow for the higher value for imidazole.

3.2. Effects of Changing Coordination Number

It is interesting to know whether the predictions of the AOM hold for different coordination numbers, especially as the complexes which the AOM is based on are in general six-coordinate, whereas many zinc-containing proteins (to which the model is applied) have four-coordinate metal ions.

Table 3 shows a series of calculations on cadmium complexes with one type of ligands at different coordination numbers. The table does not contain six-coordinate complexes because in octahedral geometry, all the elements of the NQI tensor vanish by symmetry according to the AOM.

In the AOM column, we present simple functions of ω_l (l for ligand), because the interesting point is whether the AOM predicts the trends correctly. In order to facilitate the comparison, the V_{zz}^{norm} column shows the V_{zz} values normalised by the factor ω_{zz}/ω_l from the AOM column. For example, for CdCl_2 , $\omega_{zz}/\omega_l=2$ and therefore $V_{zz}^{\text{norm}} = \frac{1}{2}V_{zz}$, so it corresponds to the partial NQI for the ligand in question. Thus, V_{zz}^{norm} should be the same for different coordination numbers, provided that the assumptions in the AOM are correct and the *ab initio* calculations are exact. Finally, $\langle V_{zz}^{\text{norm}} \rangle$ is simply the average of V_{zz}^{norm} over the various complexes.

In the chloride complexes, V_{zz}^{norm} is smaller for the two-coordinate complex than for the three-coordinate complex. This is somewhat unexpected, since the partial NQI may be interpreted as the ligand's potency to transfer charge to cadmium 5p orbitals (in addition to an ionic contribution if the ligand is charged), and it is natural to expect a decrease in this potency (and thereby a decrease of V_{zz}^{norm}) with increasing coordination number. A possible explanation of the observed increase is that the three-coordinate complex has a higher ionic contribution (it has a larger Mulliken charge on the chloride ions than the two-coordinate complex). Another possibility is that the two chloride ions in the linear CdCl_2 complex donate charge to the same 5p orbital on cadmium. Therefore, the charge transferred from each chloride ion will be less than if it were allowed to transfer charge to different 5p orbitals as in the three-coordinate complex. Based on the results presented in the section on bond length variations, we prefer the latter explanation. Consequently, two-coordinate complexes can be predicted to be representative for square planar,

Table 4. Test of ligand-ligand interactions. t, c, f, and m denote *trans*, *cis*, *facial*, and *meridional* geometries, respectively; nd means not defined. The four- and six-coordinate complexes are tetrahedral and octahedral respectively. See the text for an explanation of V_{zz}^{norm} and $\langle V_{zz}^{\text{norm}} \rangle$.

	<i>ab initio</i>		AOM		<i>ab initio</i> /AOM	
	η	V_{zz}	η	ω_{zz}	V_{zz}^{norm}	$\langle V_{zz}^{\text{norm}} \rangle$
		a. u.			a. u.	a. u.
$[\text{CdCl}_5\text{F}]^{4-}$	0.000	-0.616	0	$\omega_F - \omega_{\text{Cl}}$	0.616	
$[\text{CdCl}_4\text{F}_2]^{4-}$ t	0.000	-1.267	0	$2(\omega_F - \omega_{\text{Cl}})$	0.634	
$[\text{CdCl}_4\text{F}_2]^{4-}$ c	0.075	0.670	0	$-(\omega_F - \omega_{\text{Cl}})$	0.670	
$[\text{CdCl}_3\text{F}_3]^{4-}$ m	0.194	1.254	1	$-3/2(\omega_F - \omega_{\text{Cl}})$	0.836	0.710
$[\text{CdCl}_3\text{F}_3]^{4-}$ f	0.000	-0.059	nd	0	—	
$[\text{CdCl}_2\text{F}_4]^{4-}$ t	0.000	1.501	0	$-2(\omega_F - \omega_{\text{Cl}})$	0.751	
$[\text{CdCl}_2\text{F}_4]^{4-}$ c	0.094	-0.701	0	$\omega_F - \omega_{\text{Cl}}$	0.701	
$[\text{CdClF}_5]^{4-}$	0.000	0.766	0	$-(\omega_F - \omega_{\text{Cl}})$	0.766	
$[\text{CdCl}_3\text{F}]^{2-}$	0.000	-0.509	0	$\omega_F - \omega_{\text{Cl}}$	0.509	
$[\text{CdCl}_2\text{F}_2]^{2-}$	0.967	0.552	1	$\pm(\omega_F - \omega_{\text{Cl}})$	0.552	0.540
$[\text{CdClF}_3]^{2-}$	0.000	0.588	0	$-(\omega_F - \omega_{\text{Cl}})$	0.558	

and octahedral complexes when determining partial NQIs. As expected, V_{zz}^{norm} decreases when going from the three-coordinate complex to the four- and five-coordinate complexes.

The $[\text{CdCl}_n]^{2-n}$ complexes with more than two ligands are negatively charged. In order to test the effect of the surroundings on such negatively charged complexes we introduced a reaction field. This results in a decrease of V_{zz}^{norm} for each complex as compared to the results without reaction field, probably because the positive charges that build up near the negative chloride ions tend to balance the contribution from these ions.

For H_2O and imidazole there is no clear-cut trend for V_{zz}^{norm} as a function of the coordination number. Actually, the effect of rotating the H_2O molecules around the Cd–O axis is larger than the one found when the coordination number is changed.

In conclusion, there is no clear trend of V_{zz}^{norm} when changing the coordination number. The deviations of the individual V_{zz}^{norm} values from $\langle V_{zz}^{\text{norm}} \rangle$ are within 0.3 a. u. or about 20%. It should be noted that the bond lengths for the coordinating ligands were kept constant in these calculations in order to avoid mixing the two effects. In real complexes, the bond lengths would be expected to decrease for low coordination numbers, thereby increasing the partial NQI (see below).

3.3. Ligand–ligand Interactions

In the AOM it is assumed that the ligands do not interact, and consequently that their contributions to

	<i>ab initio</i>			AOM	<i>ab initio</i> /AOM	
	η	V_{zz}	η	ω_{zz}	V_{zz}^{norm}	$\langle V_{zz}^{\text{norm}} \rangle$
		a. u.			a. u.	a. u.
[CdClH ₂ O] ⁺	0.062	-1.951	0	$\omega_{\text{Cl}} + \omega_{\text{H}_2\text{O}}$	1.951	
CdCl ₂ (H ₂ O) ₂ c ^a	0.000	2.497	0	$-(\omega_{\text{Cl}} + \omega_{\text{H}_2\text{O}})$	2.497	2.294
CdCl ₂ (H ₂ O) ₂ t	0.921	2.435	$3 \frac{\omega_{\text{Cl}} - \omega_{\text{H}_2\text{O}}}{\omega_{\text{Cl}} + \omega_{\text{H}_2\text{O}}}$ ^b	$-(\omega_{\text{Cl}} + \omega_{\text{H}_2\text{O}})$ ^b	2.435	
CdCl ₂ (H ₂ O) ₂ tet	0.473	-1.211	1	$\pm(\omega_{\text{Cl}} - \omega_{\text{H}_2\text{O}})$	1.211	
CdCl ₂ (H ₂ O) ₄ c ^a	0.214	0.912	0	$-(\omega_{\text{Cl}} - \omega_{\text{H}_2\text{O}})$	0.912	
CdCl ₂ (H ₂ O) ₄ t	0.000	-1.799	0	$2(\omega_{\text{Cl}} - \omega_{\text{H}_2\text{O}})$	0.900	0.872
[CdCl ₄ (H ₂ O) ₂] ²⁻ c ^a	0.100	-0.640	0	$\omega_{\text{Cl}} - \omega_{\text{H}_2\text{O}}$	0.640	
[CdCl ₄ (H ₂ O) ₂] ²⁻ t	0.000	1.397	0	$-2(\omega_{\text{Cl}} - \omega_{\text{H}_2\text{O}})$	0.699	
[CdImCl] ⁺	0.066	-3.073	0	$\omega_{\text{Im}} + \omega_{\text{Cl}}$	3.073	
Cd(Im) ₂ Cl ₂ c	0.000	3.318	0	$-(\omega_{\text{Im}} + \omega_{\text{Cl}})$	3.318	3.237
Cd(Im) ₂ Cl ₂ t	0.093	3.357	$3 \frac{\omega_{\text{Im}} - \omega_{\text{Cl}}}{\omega_{\text{Im}} + \omega_{\text{Cl}}}$ ^b	$-(\omega_{\text{Im}} + \omega_{\text{Cl}})$ ^b	3.357	
Cd(Im) ₂ Cl ₂ tet	0.481	-0.235	1	$\pm(\omega_{\text{Im}} - \omega_{\text{Cl}})$	0.235	
[Cd(Im) ₂ Cl ₄] ²⁻ c ^a	0.000	0.121	0	$\omega_{\text{Im}} - \omega_{\text{Cl}}$	0.121	0.149
[Cd(Im) ₂ Cl ₄] ²⁻ t	0.207	-0.184	0	$-2(\omega_{\text{Im}} - \omega_{\text{Cl}})$	0.092	
[CdImH ₂ O] ²⁺	0.164	-2.477	0	$\omega_{\text{Im}} + \omega_{\text{H}_2\text{O}}$	2.477	
[Cd(Im) ₂ (H ₂ O) ₂] ²⁺ c	0.000	3.002	0	$-(\omega_{\text{Im}} + \omega_{\text{H}_2\text{O}})$	3.002	2.830
[Cd(Im) ₂ (H ₂ O) ₂] ²⁺ t	0.751	3.012	$3 \frac{\omega_{\text{Im}} - \omega_{\text{H}_2\text{O}}}{\omega_{\text{Im}} + \omega_{\text{H}_2\text{O}}}$ ^b	$-(\omega_{\text{Im}} + \omega_{\text{H}_2\text{O}})$ ^b	3.012	
[Cd(Im) ₂ (H ₂ O) ₂] ²⁺ tet	0.982	-1.111	1	$\pm(\omega_{\text{Im}} - \omega_{\text{H}_2\text{O}})$	1.111	
[Cd(Im) ₂ (H ₂ O) ₄] ²⁺ c ^a	0.203	1.160	0	$\omega_{\text{Im}} - \omega_{\text{H}_2\text{O}}$	1.160	1.078
[Cd(Im) ₂ (H ₂ O) ₄] ²⁺ t	0.164	-1.928	0	$-2(\omega_{\text{Im}} - \omega_{\text{H}_2\text{O}})$	0.964	

Table 5. Comparison of *ab initio* and AOM calculations in constructed cadmium complexes. tet, c, and t indicates tetrahedral, *cis*, and *trans* geometries, respectively. See the text for an explanation of V_{zz}^{norm} and $\langle V_{zz}^{\text{norm}} \rangle$.

^a An off-diagonal element is larger than 10 % of the numerically largest diagonal element. ^b ω_{zz} and η depend on the relative values of ω_A and ω_B : If $\omega_A > 2\omega_B$, then $\omega_{zz} = 2\omega_A - \omega_B$ and $\eta = \omega_B/(2\omega_A - \omega_B)$, if $2\omega_B > \omega_A > \omega_B$, then $\omega_{zz} = -(\omega_A + \omega_B)$ and $\eta = 3(\omega_A - \omega_B)/(\omega_A + \omega_B)$. Based on the *ab initio* values in Table 1 we have assumed that $2\omega_B > \omega_A > \omega_B$.

the NQI tensor are additive. In order to test this assumption we performed calculations on tetrahedral and octahedral complexes containing chloride and fluoride. These ions were chosen because the results are not obscured by effects from non-coordinating atoms. The results are presented in Table 4. As in Table 3 we present in the AOM column simple functions of ω_{Cl} and ω_{F} , and V_{zz}^{norm} is the normalised value, which in this case is an estimate of $\omega_{\text{F}} - \omega_{\text{Cl}}$. The trends in V_{zz} from the *ab initio* calculations are reasonably well reproduced by the AOM. The individual V_{zz}^{norm} deviate from the average by up to 0.18 a. u. or 26%. It is noteworthy that $\langle V_{zz}^{\text{norm}} \rangle$ is systematically larger for the octahedral complexes (0.71 a. u.) than for the tetrahedral complexes (0.54 a. u.). Furthermore, there is a tendency towards larger values of V_{zz} in complexes with many fluoride ions. This indicates that ω_{F} and ω_{Cl} depend on the coordination number, but not in the same way.

Calculations on a series of more realistic complexes involving imidazole, water, and chloride were also performed. From the results in Table 5 it can be seen that these complexes show a larger variation in V_{zz}^{norm} than the complexes in Table 4. Considering the results in Table 3, it is likely that this can be related to effects from the non-coordinating atoms. To test

this, a calculation was performed for CdCl₂(H₂O)₄ in *trans* geometry with all H₂O molecules rotated by 90° around the Cd–O axis. The result was $\eta = 0.000$ and $V_{zz} = -1.384$ a. u., which gives $V_{zz}^{\text{norm}} = 0.692$ a. u., a change of about 0.2 a. u. We conclude that the non-coordinating atoms significantly influence the EFG. This effect is not included in the current version of the AOM, but it has the potential to take such effects into account.

In conclusion, the deviations between *ab initio* and AOM results in Table 5 are caused by the combined effects of non-coordinating atoms, the coordination number, and ligand–ligand interactions, and they can amount to as much as about 0.35 a. u. (65 Mrad/s).

3.4. The Axial Symmetry Approximation

In the AOM it is assumed that the contribution to the NQI from a single ligand is axially symmetric (around the Cd–ligand axis). More precisely, the assumption is that all off-diagonal elements of the NQI (and EFG) tensor are zero, and η is zero in complexes with one ligand (and therefore also in linear two-coordinate complexes). Of course this needs not to be the case in *ab initio* calculations. From Table 1 it can be seen that chloride is the only ligand that strictly fulfills this assumption. All other complexes

have non-vanishing off-diagonal elements; the largest one is found for $\text{Cd}(\text{OH})_2$, -0.527 a. u. (14% of V_{zz}). The mean deviation of η from zero in Table 1 is 0.13.

Non-vanishing off-diagonal elements may have two effects on the EFG: 1) The principal axis system of the EFG tensor is rotated. This means that the Cd–ligand axis is no longer the appropriate z -axis to be used in the AOM-calculations. 2) The magnitude of the eigenvalues of the EFG tensor change. For $\text{Cd}(\text{OH})_2$ the z -axis was rotated by 5 degrees from the Cd–O axis and the eigenvalues changed by up to 0.05 a. u. Thus, the effect of non-vanishing off-diagonal elements seems to be relatively small. Moreover, there are indications that the deviation of η from zero may be smaller for a complex in condensed phase than in gas phase [29]. Still, caution should be exercised in complexes where the EFG tensor is sensitive to small (< 5 degrees) changes in the ligand positions.

The asymmetry parameter in Table 4 is well reproduced by the AOM in all complexes except one: $[\text{CdCl}_3\text{F}_3]^{4-}$ in meridional geometry, for which the deviation corresponds to about 0.5 a. u. for the two smallest diagonal elements of the EFG tensor. The physical reason for this large deviation might be the electrostatic repulsion between the three relatively large Cl^- ions. This may cause the total charge distribution to become more spherically symmetric, and consequently η may decrease from unity, the value predicted by the AOM. The same effect is seen to a smaller extent also in the CdA_4B_2 complexes in *cis* geometry. The effect was also observed for the CdCl_2 complex when the Cl–Cd–Cl angle was changed; when the angle decreased from 180° , the deviation between *ab initio* and AOM calculations increased, probably due to the repulsion between the two chloride charge distributions [3, 30]. Alternatively, it can be explained by charge transfer to two different cadmium 5p orbitals, whereas only one is involved in the linear molecule. The effect is probably smaller if the structure is relaxed (i. e. the geometry optimized) because the nuclei are then at their equilibrium positions.

For the more realistic complexes presented in Table 5, the largest error in the η parameter is found for the tetrahedral $\text{CdCl}_2(\text{H}_2\text{O})_2$ complex, and it is probably related to effects of the hydrogen atoms, or ligand–ligand interactions. There are also deviations for the complexes with axial symmetry (where the AOM predicts that η is zero); The mean absolute deviation of η from zero in these complexes is 0.14. This

provides an estimate of the error in η calculated by the AOM. However, it should be noted that the uncertainty in η becomes large when V_{zz} is small (because $\eta = (V_{xx} - V_{yy})/V_{zz}$) e. g. for the last three complexes containing imidazole and chloride in this table.

The deviations from axial symmetry can partly be explained by contributions from the non-coordinating ligand atoms. As discussed above, the position of the water hydrogen atoms strongly influence the calculated EFGs. For example, V_{zz} may change by 0.4 a. u. and η by 0.17 when a water or imidazole molecule is rotated around the Cd–ligand bond (see Table 5). Dynamics of the ligands at metal sites in proteins, in particular rotations around the Cd–ligand axis, may reduce the deviation from axial symmetry. In the limiting case of free rotation, axial symmetry will be fully restored. This effect might be significant for coordinating water and hydroxide, but probably not for the other ligands considered in this work. On the other hand, most protein crystal structures show that metal-bound water molecules and hydroxide ions are strongly hydrogen bonded to nearby residues, which would suppress the rotation.

Alternatively, the deviations from axial symmetry may be caused by π bonding, which is not currently included in the AOM. It is straight forward to extend the AOM to include such effects. This would require an additional parameter for each ligand, which could be extracted from *ab initio* calculations. However, it would probably be better to determine such parameters experimentally, an approach that requires PAC measurements on several additional model complexes with relevant ligands.

3.5. Effects of Varying the Cadmium–ligand Bond Length

In the AOM, the partial NQI is assumed to be independent of the Cd–ligand bond length. This assumption has been tested for Cl^- , H_2O , and imidazole.

As can be seen in Fig. 1, the partial NQI decreases as the bond length increases for all the ligands. This can be interpreted as a decrease in the charge transfer to cadmium 5p orbitals or a decrease of the ionic contribution with longer bond lengths (the Cd^{2+} ion in vacuum has a spherically symmetric charge distribution and therefore a zero EFG at the site of the nucleus).

As a first approximation, the changes can be modelled with an r^{-3} function, corresponding to a purely

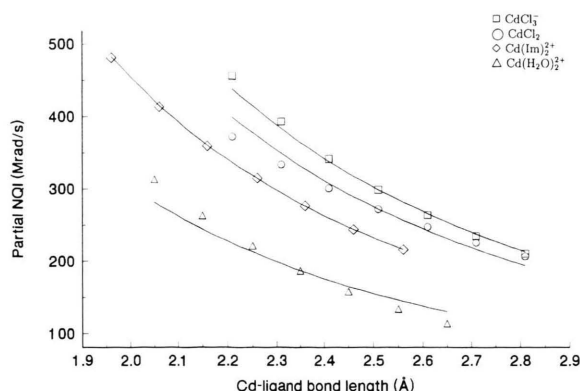


Fig. 1. Dependence of the partial NQI parameter upon the Cd-ligand bond length. The symbols correspond to *ab initio* calculations, and the full lines correspond to the approximation given in the text.

ionic model:

$$\omega_l(r) = \omega_l(r_0) \left(\frac{r_0}{r} \right)^3, \quad (3)$$

where r_0 is the normal bond length (we have used the bond lengths listed in the methods section), and $\omega_l(r_0)$ is the calculated partial NQI at that bond length (it should be noted that the AOM is based on molecular orbital theory and is therefore not a point ion model).

Quite unexpectedly, this simple model accounts for most of the changes of the partial NQI, as can be seen in Figure 1. This suggests that (3) may be used for all ligands, making it immediately applicable in the AOM: If a ligand is not found at the bond length r_0 , the partial NQI is simply scaled by $(r_0/r)^3$.

Equation (3) is an important improvement of the AOM because changes of bond lengths by up to 0.2 Å occur, depending on the coordination number and the charge of the ligands. According to Fig. 1, such variations can lead to changes in the partial NQIs of up to 100 Mrad/s, or 30%. Furthermore, it allows for the assignment of partial NQIs to ligands at unusual distances from the metal ion, as for example the methionine ligand in the blue copper protein azurin [31].

For chloride, both two- and three-coordinate complexes were investigated. Surprisingly, the partial NQI for the three-coordinate complexes increased more than for the two-coordinate complexes upon shortening of the bond. This could be interpreted as a relatively larger ionic contribution at shorter bond lengths with three than with two ligands, an interpretation that is supported by the fact that the two complexes give approximately the same partial NQI at long bond

length (the ionic contribution). However, two things talk against this. Firstly, an ionic contribution of 200 Mrad/s at a bond length of 2.81 Å is extreme, corresponding to a charge of $-2.7 e$ (using a Sternheimer shielding constant of -29.3 [32]). Secondly, the difference in Mulliken charge between the chloride ions in the two complexes does not change significantly with distance.

An alternative explanation is that the chloride ions in the three-coordinate complexes are capable of transferring more charge per ligand to the cadmium 5p orbitals, and that this effect increases with shorter bond lengths. As mentioned earlier, this may be caused by a competition between the two chloride ions in CdCl_2 for the same 5p orbital on cadmium.

3.6. Concluding Remarks

We have made a critical assessment of the assumptions which constitute the basis of the AOM for the calculation of NQIs of cadmium-containing complexes. The results show that the AOM can be improved in several ways. First, we suggest a simple rule to correct the partial NQI for variations in the Cd-ligand bond length, (3). Second, we have determined a value for hydroxide ligands, $\omega_{\text{OH}^-} = 349$ Mrad/s. Third, the partial NQI for histidine ligands might need to be changed. This will be further investigated in a forthcoming publication. Fourth, non-coordinating atoms (e.g. hydrogens in water and carbons and hydrogens in imidazole) significantly affect the NQI of a complex. Such effects can be included in the AOM with some effort, but the present results indicate that it may be worthwhile. Fifth, the coordination number and ligand-ligand interactions may also lead to errors in the AOM, but these effects seem to be less important than those from non-coordinating atoms. Finally, our results indicate that the assumption of axial symmetry works well in most complexes.

In total, our results indicate that the uncertainty in the AOM is less than 50 Mrad/s in most cases, but can be up to 100 Mrad/s (0.5 a.u.) for the diagonal elements of the NQI tensor. However, it should be noted that the AOM has been successfully applied to several biological systems with smaller errors (average error of about 30 Mrad/s [11, 33–35]). This may be an effect of cancelation of errors or that the AOM works better for proteins and crystalline complexes (for which it was optimised) than for small model systems in vacuum.

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- [1] A. Lerf and T. Butz, *Hyperfine Interactions* **36**, 275 (1987).
- [2] T. Soldner, W. Tröger, T. Butz, P. Blaha, and K. Schwarz, *Z. Naturforsch.* **53a**, 411 (1998).
- [3] L. Hemmingsen and U. Ryde, *J. Phys. Chem.* **100**, 4803 (1996).
- [4] D. P. van der Werf, H. van Leuken, and R. A. de Groot, *Phys. Rev. B* **52**, 3909 (1995).
- [5] B. Lindgren and A. Ghandour, *Hyperfine Int.* **78**, 291 (1993).
- [6] B. Lindgren, *Europhys. Lett.* **11**, 555 (1990).
- [7] P. Blaha, K. Schwarz, and P. H. Dederichs, *Phys. Rev. B* **37**, 2792 (1988).
- [8] U. Ryde and L. Hemmingsen, *J. Biol. Inorg. Chem.* **2**, 567 (1997).
- [9] T. P. Das, and P. C. Schmidt, *Z. Naturforsch.* **41a**, 47 (1987); and references therein.
- [10] R. Weht, G. Fabricius, M. Weissmann, M. Renteria, C. P. Massolo, and A. G. Bibiloni, *Phys. Rev. B* **49**, 14939 (1994).
- [11] R. Bauer, S. J. Jensen, and B. Schmidt-Nielsen, *Hyperfine Int.* **39**, 203 (1988).
- [12] P. C. Schmidt, A. Weiss, S. Cabus, and J. Kübler, *Z. Naturforsch.* **42a**, 1321 (1987).
- [13] C. E. Schaeffer, *Struct. Bond.* **5**, 68 (1968).
- [14] R. Bauer, H. W. Adolph, I. Andersson, E. Danielsen, G. Formicka, and M. Zeppezauer, *Eur. Biophys. J.* **20**, 215 (1991).
- [15] E. Danielsen, R. Bauer, L. Hemmingsen, M.-L. Andersen, M. J. Bjerrum, T. Butz, W. Tröger, G. W. Canters, C. W. G. Hoitink, G. Karlsson, Ö. Hansson, and A. Messerschmidt, *J. Biol. Chem.* **270**, 573 (1995).
- [16] B. M. Craven, R. K. McMullan, J. D. Bell, and H. C. Freeman, *Acta Cryst. B* **33**, 2585 (1977).
- [17] W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956).
- [18] *Insight II*, version 2.3.0: Biosym Technologies, San Diego 1993.
- [19] V. Kellö and A. J. Sadlej, *Theor. Chim. Acta* **91**, 353 (1995).
- [20] W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).
- [21] P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.* **66**, 217 (1972).
- [22] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, and J. A. Pople, *J. Chem. Phys.* **77**, 3654 (1982).
- [23] A. M. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, G. A. Kieth, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, *Gaussian 94* (Revision D.1 and D.4). Gaussian, Inc., Pittsburgh PA 1995.
- [24] K. Andersson, M. P. Fülscher, G. Karlström, R. Lindh, P.-Å. Malmqvist, J. Olsen, B. O. Roos, A. J. Sadlej, M. R. A. Blomberg, P. E. M. Siegbahn, V. Kellö, J. Noga, M. Urban, and P.-O. Widmark *MOLCAS* version 3 (1994), Dept. of Theor. Chem., Chem. Centre, University of Lund, P.O.B. 124, S-221 00 Lund, Sweden.
- [25] H. L. Friedman, *Mol. Phys.* **29**, 1533 (1975).
- [26] P. Herzog, K. Freitag, M. Reuschenbach, and H. Walitzki, *Z. Phys. A* **294**, 13 (1980).
- [27] P. Raghavan, *Atom. Data Nucl. Data Tab.* **42**, 189 (1989).
- [28] R. Candlin and M. M. Harding, *J. Chem. Soc. A*, 421 (1967).
- [29] T. Soldner, *Diplomarbeit* (in German), University of Leipzig, Dept. of Physics and Earth Sciences, Nuclear Solid State Physics section, Linné Strasse 5, D-04103 Leipzig, Germany (1996).
- [30] L. Hemmingsen, Ph.D.-thesis, The Agricultural University, Dept. of Mathematics and Physics, Thorvaldsensvej 40, 1871 FRB C, Denmark, (1995).
- [31] H. Nar, A. Messerschmidt, R. Hubert, M. van de Kamp, and G. W. Canters, *J. Mol. Biol.* **221**, 765 (1991).
- [32] F. D. Feiock, and W. R. Johnson, *Phys. Rev.* **187**, 39 (1969).
- [33] L. Hemmingsen, R. Bauer, M. J. Bjerrum, M. Zeppezauer, H. W. Adolph, G. Formicka, and E. Cedergren-Zeppezauer, *Biochemistry* **34**, 7145 (1995).
- [34] R. Bauer, E. Danielsen, L. Hemmingsen, M. V. Sørensen, J. Ulstrup, E. P. Friis, D. Auld, and M. J. Bjerrum, *Biochemistry* **36**, 11514 (1997).
- [35] E. Danielsen, R. Bauer, L. Hemmingsen, M.-L. Andersen, M. J. Bjerrum, T. Butz, W. Tröger, G. W. Canters, C. W. G. Hoitink, G. Karlsson, Ö. Hansson, and A. Messerschmidt, *J. Biol. Chem.* **270**, 573 (1995).