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Gauge origin independence in finite basis sets and perturbation theory

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Abstract

We show that origin independence in finite basis sets for the oscillator strengths is possibly in any gauge contrary to what is stated in literature. This is proved from a discussion of the consequences in perturbation theory when the exact eigenfunctions and eigenvalues to the zeroth order Hamiltonian H_0 cannot be found. We demonstrate that the erroneous conclusion for the lack of gauge origin independence in the length gauge stems from not transforming the magnetic terms in the multipole expansion leading to the use of a mixed gauge. Numerical examples of exact origin dependence are shown.

Keywords: Gauge origin independence, Finite basis sets, Perturbation theory, Oscillator Strengths, X-ray Spectroscopy

1. Introduction

Gauge freedom is a fundamental part of modern physical theories and these theories allows for a range gauge transformations which changes the potential but leaves the fields unaltered. For exact solutions of the Hamiltonian the choice of gauge does not matter, however, once approximations are introduced significant differences between different gauges can be observed and the choice of gauge can therefore become imperative. For calculations in atomic and molec-

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ular physics and chemistry usually the Coulomb gauge along with either the velocity or length gauge is chosen. Here the Coulomb gauge regulates the redundant degrees of freedom by fixing the relation between the scalar ϕ and vector \mathbf{A} potentials while the length or velocity gauges gives the mathematical identification of the electric \mathbf{E} and magnetic \mathbf{B} fields. We will here show that the usual formulas in literature given for the multipole expansion beyond the dipole approximation in the length gauge are in fact in a mixed gauge where the electric parts are in the length gauge while the magnetic parts are in the velocity gauge. While the use of the mixed gauge does not matter for exact solutions of the Hamiltonian this can, however, affect the origin independence of the observables in finite basis sets. The mixed gauge has furthermore lead to the erroneous conclusion that origin independence for the multipole expansion in finite basis sets is only possible in the velocity gauge [1, 2, 3]. We will here show that origin independence in the length gauge is also possible finite basis sets.

In perturbation theory the effect of a perturbation is usually derived assuming that the exact eigenfunctions and eigenvalues for the zeroth order Hamiltonian \hat{H}_0 are known [4, 5]. For systems like a particle in a box, the harmonic oscillator and other systems which can be solved algebraically the exact eigenfunctions and eigenvalues can of course be obtained, however, for most applications of perturbation theory the exact eigenfunctions and eigenvalues of \hat{H}_0 are not known. Examples of this, related to electronic structure theory, is the inclusion of an external electromagnetic field that perturbs an atom or molecule, since it is here assumed that the exact time-independent solution of the atom or molecule is known, or even describing the electron correlation with perturbation theory, such as Møller-Plesset perturbation theory [6], since the SCF equations are solved in a finite basis set. The consequences of not having the exact eigenfunctions and eigenvalues of \hat{H}_0 are rarely discussed if at all [7, 8]. Examples are therefore often presented for exactly solvable quantum systems while for systems where the exact eigenvalues and eigenfunctions cannot be found the connection to the assumption of exact eigenvalues and eigenfunctions are rarely

discussed. We will here demonstrate that even if gauge invariance is lost due to approximations origin independence for the multipole expansion will still be conserved in the different gauges.

When the focus is on \hat{H}_0 the aim is to construct a better \hat{H}_0 [9, 10] and not if the exact solution to the given \hat{H}_0 can be found. Usually the the focus in perturbation theory has been on the development of new types of perturbation expansions [11, 6, 12], their relations [13], the convergence [14] or lack thereof [15, 16, 17], bound for the energies [18], eliminating of intruder states [19, 20], conceptual developments of effective Hamiltonians [21, 22, 23], multiconfigurational [24, 25] or degenerate perturbation theory [26, 27, 28] just to mention a few of the many developments that has been on perturbation theory over many years. For a more detailed historical account of the development of perturbation theory we refer to Löwdins work on this [29].

We will here show that in perturbation theory it can be useful to consider the initially found eigenvalues and eigenfunctions found after the introduction of the approximations as exact eigenvalues and eigenfunctions of some approximate or effective zeroth order Hamiltonian \hat{H}'_0 . In this way the exact eigenfunctions and eigenvalues are always found though not for the exact \hat{H}_0 but for the approximate \hat{H}'_0 . Always having the exact solution to \hat{H}'_0 means that any perturbation statement will always be true for any choice of basis set and level of correlation provided that the perturbation statement is based on a perturbation expansion which only require that \hat{H}'_0 has a spectrum and not on some intrinsic properties of \hat{H}_0 . An example of a perturbation statement is the origin independence of higher order intensities [2], where an external electromagnetic field is applied to a molecular system, and the perturbation treatment is performed using Fermi's golden rule.

We will exploit the simple observation that the exact eigenfunctions and eigenvalues for \hat{H}'_0 is always known to show that the origin independence of higher order intensities [2] always hold in both the velocity and length gauge. It will be shown that the reported problems with origin independence in the length gauge in finite basis sets stems from derivations using a mixed gauge [1, 2, 3].

These findings will be backed by some numerical examples of exact and approximate origin dependence for certain electric and magnetic contributions to the origin independent intensities [2] for $[\text{FeCl}_4]^{1-}$ in the velocity, length and mixed gauge [1]. That the intensities are origin independent in the velocity gauge in approximate calculations have been numerically observed before [2, 3, 30]. We will here show the reason why this is always true and explain why this is not only true for the velocity gauge but also in the length gauge.

The calculation of the intensities presented here can be performed significantly more elegant by calculating the exact expression, from Section ?? in the supplementary material, as shown by List et al.[30, 31]. Here the multipole expansion is completely avoided and origin independence is also a given in the velocity gauge, as also discussed in Section ??.

2. Theory

In the first two parts of this section we will discuss perturbation theory, with a particular focus on how the the zeroth order Hamiltonian \hat{H}_0 is constructed and what kind of consequences this has for the perturbation expansion. We will here show that the \hat{H}_0 usually assumed used is in fact approximated by \hat{H}'_0 and as a consequence the exact eigenfunctions and eigenvalues of the used zeroth order Hamiltonian \hat{H}'_0 is trivially found. An example from Configuration-Interaction (CI) theory [32] on how a series of approximate Hamiltonians can be constructed from the exact solution is shown in Section ??.

Thereafter we will use the findings from the construction of approximate Hamiltonians to show that the so-called quadrupole intensities, recently derived by Bernadotte et al.[2], will be origin independent in both the velocity and length gauge irrespectively of the choice of basis set and level of correlation. Here we will repeat the equations essential to show origin independence for self consistency in Sections ?? to ??, illustrate where \hat{H}'_0 enters, where the error in literature for the multipole expansion in the length gauge enters and what the correct expression should be and finally show why the different gauges always

will show exact origin independence. When missing we refer to the excellent work by Bernadotte et al.[2] for complete derivations of the origin independent intensities in the velocity gauge.

2.1. Perturbation theory

In perturbation theory the Hamiltonian \hat{H} is divided into a zeroth order Hamiltonian \hat{H}_0 and a perturbation \hat{U}

$$\hat{H} = \hat{H}_0 + \hat{U} \quad (1)$$

where it is assumed that the exact eigenfunctions and eigenvalues for \hat{H}_0 are known and that the effect of \hat{U} in some sense is sufficiently small so that the eigenfunctions of \hat{H} can be expanded in the eigenfunctions of \hat{H}_0 . The perturbation \hat{U} is, however, independent of \hat{H}_0 so an alternative Hamiltonian \hat{H}' with the same perturbation \hat{U}

$$\hat{H}' = \hat{H}'_0 + \hat{U}, \quad (2)$$

where again it is assumed that the exact eigenfunctions and eigenvalues for \hat{H}'_0 are known, is also acceptable.

Any conclusion reached for a perturbation expansion will always be true of any choice of \hat{H}_0 or \hat{H}'_0 , which only require knowledge of the exact eigenfunctions and eigenvalues of \hat{H}_0 or \hat{H}'_0 , provided that \hat{H}_0 and \hat{H}'_0 has a spectrum and the perturbation treatment does not depend on some intrinsic property of \hat{H}_0 or \hat{H}'_0 . In the latter case the perturbation expansions will then only be identical for another \hat{H}_0 or \hat{H}'_0 with the same intrinsic properties. The intrinsic property of \hat{H}_0 could be some special commutation relations with \hat{U} that would simplify the perturbation expansion or give some special conclusion which for example could happen if \hat{U} is a function of \hat{H}_0 . We will here limit ourselves to perturbation expansions which do not depend on any intrinsic properties of \hat{H}_0 and hence the choice of \hat{H}_0 can be chosen independently of \hat{U} .

As an example of this freedom one can even choose to include some fictitious interaction in \hat{H}_0 ,

$$\hat{H} = \hat{H} - \hat{H}_{fic} + \hat{H}_{fic} = \hat{H}_0 + \hat{H}_{fic} = \hat{H}_0 + \hat{U} \quad (3)$$

where \hat{H}_{fic} is some fictitious interaction. If the exact eigenfunctions for \hat{H}_0 in Eq. 3 can be found, make sense and give a convergent perturbation series then this can be a practical way of solving the eigenvalue problem for \hat{H} .

While it may seem strange to introduce some fictitious interaction the well known Møller-Plesset perturbation theory [6] where the perturbation operator $\hat{\Phi}$, known as the fluctuation operator,

$$\hat{\Phi} = \hat{H} - \hat{f} - h_{nuc} \quad (4)$$

has the artificial mean-field description from Hartree-Fock \hat{f} subtracted can be formulated as such.

2.2. Approximations and exact eigenfunctions

In all perturbation calculations \hat{H}_0 is in some way approximated except for those where an algebraic solution is known like the harmonic oscillator, particle in a box et cetera. The two major approximation usually performed in electronic structure theory is the projection of the wavefunction onto a finite basis and the second in the interaction between particles like truncating the CI hierarchy. These approximations are usually thought of as approximations in the wavefunction for the exact Hamiltonian but they are in fact a way of creating an approximate or effective zeroth order Hamiltonian \hat{H}'_0 which is solved exactly

$$\hat{H}_0 = \hat{H}_0 - \hat{H}'_0 + \hat{H}'_0 = \hat{H}'_0 + \hat{H}_{rest} \quad (5)$$

where the remaining effects from the finite basis and incomplete correlation treatment are incorporated in \hat{H}_{rest} . It may not be directly possible to write down \hat{H}_{rest} for a specific system in a closed form, the division of the Hamiltonian in Eq. 5 is, however, still allowed.

When performing calculations it is the approximate zeroth order Hamiltonian \hat{H}'_0 that will be solved and not \hat{H}_0 . Hence it is not the exact Hamiltonian \hat{H} in Eq. 1 that is being solved but the approximate or effective Hamiltonian \hat{H}' in Eq. 2 when a perturbation is applied to the system. Any perturbation

derivation and conclusions should therefore be based on \hat{H}'_0 and not \hat{H}_0 since \hat{H}'_0 is the zeroth order Hamiltonian used in calculations.

In electronic structure theory the part of \hat{H}_{rest} concerned with the electron correlation in the finite basis set used by \hat{H}'_0 is often used as a perturbation \hat{U} to improve the description of the electronic structure [11, 6, 12]. Even if a finite basis set for \hat{H}'_0 is used all of \hat{H}_{rest} can in principle be recovered in perturbation theory by using a complete basis for \hat{H}_{rest} [7]. The idea of having a different basis set in the SCF or CASSCF and the subsequent perturbation expansion have been explored before [33, 34] and was motivated by the fact that higher angular momentum functions is significantly more important in the perturbation treatment of the dynamic correlation compared to the static correlation in the SCF or CASSCF calculation.

The approximate Hamiltonian \hat{H}'_0 can then be perturbed with \hat{U} as shown in Eq. 2 in order to find a perturbation solution to \hat{H}' . Since the exact eigenfunctions to \hat{H}'_0 will always be found by construction and all effects of the finite basis and incomplete correlation treatment is in \hat{H}_{rest} then any conclusions based on the perturbation treatment therefore does not depend on the size of the basis set or the level of correlation treatment. While the perturbation \hat{U} is written as the same in Eqs. 1 and 2 the effect of \hat{U} will be affected by the choice of \hat{H}'_0 and hence the result of the perturbation will differ. An example of creating an effective Hamiltonian is given in Section ??.

2.3. Origin independence of the oscillator strengths

We will in this section briefly sketch the perturbation inclusion of weak electromagnetic fields and origin independence with the aim is showing how \hat{H}'_0 enters, why both the velocity and length gauge always show origin independence in quantum chemical calculations and finally to show the equations illustrated in the applications in Sec. 3. Here we will show that both the electric and magnetic terms will exhibit exact origin dependence in both the length and velocity gauge.

It is throughout assumed that the electromagnetic fields are weak and can be

treated as a perturbation of the molecular system which in our case is described by the Schrödinger equation within the Born-Oppenheimer approximation

$$\hat{H}_0 = \sum_{i=1}^N \frac{\hat{\mathbf{p}}_i^2}{2m_e} + V(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (6)$$

where $\hat{U}(t)$ is the time-dependent perturbation

$$\hat{U}(t) = \frac{eA_0}{2m_e c} \sum_i \exp(i(\mathbf{k} \cdot \mathbf{r}_i - \omega t)) (\mathcal{E} \cdot \hat{\mathbf{p}}_i) \quad (7)$$

from a monochromatic linearly polarized electromagnetic wave. In Eq. 7 \mathbf{k} is the wave vector pointing in the direction of propagation, \mathcal{E} the polarization vector perpendicular to \mathbf{k} , ω is the angular frequency and A_0 the amplitude of the vector potential.

By applying Fermi's golden rule and assuming that transitions only occur when the energy difference between the eigenstates of the unperturbed molecule matches the frequency of the perturbation

$$\omega = \omega_{0n} = \frac{E_n - E_0}{\hbar} \quad (8)$$

the explicit time dependence can be eliminated from the transition rate

$$\Gamma_{0n}(\omega) = \frac{2\pi}{\hbar} |\langle 0 | \hat{U} | n \rangle|^2 \delta(\omega - \omega_{0n}) = \frac{\pi A_0^2}{2\hbar c} |T_{0n}|^2 \delta(\omega - \omega_{0n}). \quad (9)$$

In Eq. 9 the relation between the transition moments T_{0n} and the time-independent part of \hat{U} in Eq. 7 is seen. The effect of the weak electromagnetic field can now be expressed as a time-independent expectation value.

Demonstrating origin independence for the oscillator strengths f_{0n}

$$f_{0n} = \frac{2m_e}{e^2 E_{0n}} |T_{0n}|^2, \quad (10)$$

where $E_{0n} = E_n - E_0$ is the difference in the eigenstates of the unperturbed molecule, for Eq. 7 for the exact solution in any gauge is often showed in textbooks. We have repeated the proofs in Section ?? in order to show that origin independence for the exact expression in Eq. 7 also will hold for finite basis sets.

Bernadotte et al.[2] showed that origin independence in the oscillator strengths f_{0n} for the multipole expansion of Eq. 7 comes naturally provided that the collection of the terms in Taylor expansion of the exponential of the wave vector \mathbf{k} in Eq. 7 are collected to the same order in the observable oscillator strengths in Eq. 10

$$\begin{aligned} f_{0n} &= f_{0n}^{(0)} + f_{0n}^{(1)} + f_{0n}^{(2)} + \dots \\ &= \frac{2m_e}{e^2 E_{0n}} |T_{0n}^{(0)} + T_{0n}^{(1)} + T_{0n}^{(2)} + \dots|^2 \end{aligned} \quad (11)$$

and not in the transition moments T_{0n} traditionally done. As first demonstrated by Lestrangle et al.[3] collecting the terms in the oscillator strengths according to Eq. 11 does not ensure that the total oscillator strength is positive when truncating the expansion. The total negative oscillator strengths when truncating Eq. 11 appear to be a basis set problem that can occur for unbalanced basis sets [1] where the transition integrand is poorly described [35].

In the derivation of Fermi's golden rule only the knowledge of the exact eigenfunctions and eigenvalues of \hat{H}_0 are required. There is no requirement that a specific \hat{H}_0 must be used nor does the result depend on any intrinsic properties of \hat{H}_0 . Because of this will any equations derived using \hat{H}_0 from Eq. 1 or \hat{H}'_0 from Eq. 2 only differ in the eigenfunctions and eigenvalues used and therefore any conclusions, like origin independence, will also be valid for \hat{H}'_0 , irrespectively of the choice of basis set or level of correlation treatment.

Since \hat{H}'_0 in general is not gauge invariant the gauge should be fixed before any approximations are made. Using the hypervirial theorem [36] in the transformation from the velocity gauge to the length gauge with \hat{H}'_0 as shown in Section ?? can be used to check the quality of the basis set and correlation method with respect to gauge transformations. The transformation of \hat{H}'_0 is not a direct measure of which gauge best describes a given transition with the chosen basis and correlation method set but will likely spot potential numerical problems for transition moments since the integrand is different in different gauges.

The origin independence of the multipole expansion beyond the dipole ap-

proximation relies on the exact cancellation of several terms which are all origin dependent. The terms up to the quadrupole oscillator strengths are given in Section ?? and the origin dependence in Section ?. If the exact eigenfunctions for \mathbf{H}_0 in Eq. 6 were required for exact origin dependence deviations from this would be easy to see numerically in low level quantum chemistry calculations simply by moving the origin.

2.4. Mixed gauge and origin independence in the length gauge

We will here briefly repeat the multipole expansion in the length gauge in order to demonstrate that origin independence in the length gauge does not only hold for the exact semi-classical expression as shown in Section ?? but also for the multipole expansion. Secondly we also wish to show the correct expressions for the different terms in the multipole expansion in the length gauge and show how the mixed gauge enters.

Inserting the multipole expansion

$$\exp(i\mathbf{k} \cdot \mathbf{r}_i) = (1 + i(\mathbf{k} \cdot \mathbf{r}_i) - \frac{1}{2}(\mathbf{k} \cdot \mathbf{r}_i)^2 + \dots) \quad (12)$$

into the exact semiclassical expression in length gauge from Eq. ?? the different orders can be identified

$$T_{0n}^{(0)} = -i\frac{1}{\hbar}\langle 0|\mathcal{E} \cdot [\mathbf{r}, \hat{\mathbf{H}}_0]|n\rangle = -i\frac{E_{0n}}{\hbar}\langle 0|\mathcal{E} \cdot \mathbf{r}|n\rangle \quad (13)$$

$$T_{0n}^{(1)} = \frac{e}{\hbar} \sum_i \langle 0|i(\mathbf{k} \cdot \mathbf{r}_i)(\mathcal{E} \cdot [\mathbf{r}_i, \hat{\mathbf{H}}_0])|n\rangle \quad (14)$$

$$T_{0n}^{(2)} = -\frac{e}{2\hbar} \sum_i \langle 0|i(\mathbf{k} \cdot \mathbf{r}_i)^2(\mathcal{E} \cdot [\mathbf{r}_i, \hat{\mathbf{H}}_0])|n\rangle \quad (15)$$

$$T_{0n}^{(3)} = \dots \quad (16)$$

The zero order term is easily identified as the transition dipole moment in the length gauge. The first order terms can be identified in the usual way where these are divided into terms that are symmetric and anti-symmetric with respect to interchanging the wave vector \mathbf{k} and polarization vector \mathcal{E}

$$T_{0n}^{(1)} = \frac{e}{\hbar} \sum_i \langle 0|i(\mathbf{k} \cdot \mathbf{r}_i)(\mathcal{E} \cdot [\mathbf{r}_i, \hat{\mathbf{H}}_0])|n\rangle \quad (17)$$

$$= \frac{e}{2\hbar} \sum_i (\langle 0 | (\mathbf{k} \cdot \mathbf{r}_i) ([\mathbf{r}_i, \hat{\mathbf{H}}_0] \cdot \mathcal{E}) + (\mathbf{k} \cdot [\mathbf{r}_i, \hat{\mathbf{H}}_0]) ((\mathbf{r}_i \cdot \mathcal{E}) | n \rangle \quad (18)$$

$$+ \langle 0 | (\mathbf{k} \cdot \mathbf{r}_i) ([\mathbf{r}_i, \hat{\mathbf{H}}_0] \cdot \mathcal{E}) - (\mathbf{k} \cdot [\mathbf{r}_i, \hat{\mathbf{H}}_0]) ((\mathbf{r}_i \cdot \mathcal{E}) | n \rangle) \quad (19)$$

$$= \frac{E_{0n}}{2\hbar} k_\alpha \mathcal{E}_\beta \langle 0 | e \sum_i r_{i,\alpha} r_{i,\beta} | n \rangle \quad (20)$$

$$+ \frac{e}{2\hbar} (\mathbf{k} \times \mathcal{E}) \sum_i \langle 0 | (\mathbf{r}_i \times [\mathbf{r}_i, \hat{\mathbf{H}}_0]) | n \rangle \quad (21)$$

$$= T_{0n}^Q + T_{0n}^{m^l}. \quad (22)$$

From the symmetric part the electric quadrupole transition moment and for the anti-symmetric part the magnetic dipole transition moment in the length gauge appears.

When presenting the magnetic dipole transition moment in Eq. 21 in literature the hypervirial theorem [36] from Eq. ?? is not invoked for the magnetic part. This, however, corresponds to transforming the electric terms to the length gauge while leaving the magnetic terms in the velocity gauge which gives a mixed gauge. This mixed gauge is presented as the length gauge in literature or the discussion of gauge is not present.

If \hat{H}_0 is solved exactly using a mixed gauge will not cause any problems since the individual terms in the multipole expansion in the velocity and length gauge will be identical. In finite basis sets the individual terms will not be identical since the integrand in the different gauges will be different [35]. The mixed gauge has therefore lead to the erroneous conclusion that origin independence only is possible in the velocity gauge since for the magnetic terms in length gauge electric terms in the velocity gauge appears (see Eqs. ?? and ??) when the origin is moved [1, 2, 3]. Keeping the magnetic dipole transition moment in the velocity gauge is very understandable from both a theoretical and numerical perspective since the terms in this way all will look like the familiar terms from electrodynamics and the integrals will be more readily available in quantum chemistry codes. The use of the mixed gauge should, however, be used with caution since this is exactly why origin independence could not be achieved in a previous application [1].

When using the proper expression for the magnetic dipole transition moment in the length gauge, as shown in Eq. 21, it is easy to show that lower order terms arising from the movement of the origin will all be in the length gauge

$$T_{0n}^{m^l}(\mathbf{O} + \mathbf{a}) = \sum_i \langle 0 | ((\mathbf{r}_i - \mathbf{a}) \times [(\mathbf{r}_i - \mathbf{a}), \hat{\mathbf{H}}_0]) | n \rangle \quad (23)$$

$$= \sum_i \langle 0 | \mathbf{r}_i \times [\mathbf{r}_i, \hat{\mathbf{H}}_0] - \mathbf{a} \times [\mathbf{r}_i, \hat{\mathbf{H}}_0] \quad (24)$$

$$+ \mathbf{r}_i \times [-\mathbf{a}, \hat{\mathbf{H}}_0] + \mathbf{a} \times [\mathbf{a}, \hat{\mathbf{H}}_0] | n \rangle \quad (25)$$

$$= T_{0n}^{m^l}(\mathbf{O}) - \varepsilon_{\alpha\beta\gamma} a_\beta E_{0n} \sum_i \langle 0 | r_{i,\gamma} | n \rangle. \quad (26)$$

The translation of the origin now no longer gives the electric dipole moment in velocity gauge but length gauge so there is no longer any inter gauge dependence. Since the momentum operator does not appear in the magnetic terms in the length gauge it is evident that also for all higher order magnetic terms all lower order terms arising from translation of the coordinate system will be in the length gauge. In the hypervirial theorem local potentials are assumed and therefore no two-electron integrals will appear in the commutator

$$[r, \hat{H}_0] = [r, \hat{T}] \iff [r, V] = 0 \quad (27)$$

where \hat{T} is the kinetic energy operator.

Since the inter gauge dependence for the magnetic terms have been removed the derivation of the origin independence shown by Bernadotte et al.(see Appendix C in [2]) can be repeated for the multipole expansion in the length gauge and exact cancellation in the oscillator strength order for order is therefore also possible for finite basis sets in the length gauge. Any method will show exact origin independence also in finite basis sets in both the velocity and length gauge though the different gauges introduces a constant gauge difference for every individual transition. The best gauge in a finite basis set will completely depend on how well the integrand is represented in the given basis set. For different transitions in the same finite basis the best gauge may not be the same for all transitions.

The choice of Coulomb gauge regulate the redundant degrees of freedoms, in our case, in the electromagnetic fields and the length or velocity gauge gives the mathematical expression for the fields and since gauge transformations in finite basis sets for effective Hamiltonians are not exact the gauge should be chosen before any approximations. In Section ?? this is discussed in a bit more detail along with the usual way of applying the hypervirial theorem in gauge transformations between the length and velocity gauge.

3. Application

To numerically prove the exact origin independence in any gauge for any basis set or level of correlation we will use the recently implemented origin independent quadrupole intensities part in MOLCAS [1, 37]. Since our implementation is in a mixed gauge and $f_{0n}^{(\mu^2)}$ is the only electric term implemented in both the velocity and length gauge our implementation does not show exact origin independence unlike those where the velocity gauge is used [2, 30, 31, 3]. However, since the origin independence relies on exact cancellation it is sufficient to show the exact origin dependence of the different terms in Section ?? with the exact origin dependence shown in Section ?? for the $[\text{FeCl}_4]^{1-}$ molecule using different basis sets and level of correlation. Because of the mixed gauge implementation exact origin dependence is only shown for the electric terms in the length gauge and magnetic terms in the velocity gauge.

3.1. Computational details

We have chosen the $[\text{FeCl}_4]^{1-}$ molecule due to its significant increase in pre-edge intensity, through 4p mixing, in X-ray absorption spectroscopy (XAS) [38, 39]. The 4p mixing gives rise to very large $f_{0n}^{(\mu^2)}$ and hence makes the terms in Eqs. ??-?? grow significantly faster and thereby making the conservation of origin independence more difficult [1].

We have throughout used the ANO-RCC basis sets [40, 41] since these basis sets have been shown to perform reasonably well in conserving the origin independence in the mixed gauge for the quadrupole intensities [1]. Furthermore

we have included AUG-cc-pVDZ [42, 43] basis set, which in a previous application on $[\text{FeCl}_4]^{1-}$ gave unphysical results, to show that good basis sets are not needed to have exact origin independence in any gauge but that the mixed gauge is very sensitive to this.

For the correlation treatment all calculations will be at the RASSCF level, since the FCI limit cannot be reached, with the 1s core electrons in RAS1 and 11 electrons in 13 orbitals in RAS2. Here $[\text{FeCl}_4]^{1-}$ will have T_d geometry with an Fe-Cl distance of 2.186 Å and the orbitals for the core-excited states will be averaged over 70 states. The intensities are calculated using the RASSI program [44, 45] which uses a biorthonormalization procedure which removes the gauge dependence of non-orthogonal states.

While the Hamiltonian used in the derivation of the intensities in Sec. 2.3 is based on the Schrödinger equation we will use a second-order Douglas-Kroll-Hess Hamiltonian [46, 47] to take into account the scalar relativistic effects, however, as shown in Sec. 2.2 the choice of \hat{H}_0 does not matter.

While it would be sufficient only to run two calculations with different origins to show that the quadrupole intensities are origin independent in the any gauge we will try to vary the basis set to illustrate the point that the perturbation does depend on the choice of \hat{H}_0 , as stated in Sec. 2.2, and that in the mixed gauge presented in literature is very sensitive to the choice of basis set. We will therefore show calculations illustrating the exact origin dependence of the electric terms in the mixed gauge along with the exact origin dependence of $f_{0n}^{(m^2)}$ in the velocity gauge and the basis set dependence in the mixed gauge. To show the exact origin dependence a calculation with the origin shifted \mathbf{a} away from the Fe atom will be compared to a calculation with a calculation where the origin is placed on the Fe atom and the effect of shifting the origin with \mathbf{a} is calculated using Eqs. ??-??. This essentially means comparing the left and right hand side of Eqs. ??-??.

3.2. Electric terms

As shown in Eq. ?? the origin dependence of $f_{0n}^{(Q^2)}$ in the length gauge is exact, up to numerical rounding, in the approximate calculations performed in electronic structure theory. In Figure 1 $f_{0n}^{(Q^2)}$ for the third core excited state in the length gauge in different basis sets have been plotted. The third core excited state was selected due to the very large $f_{0n}^{(\mu^2)}$. $f_{0n}^{(Q^2)}$ is seen to increase rapidly as the origin is moved in the Z -direction which is due to the very large $f_{0n}^{(\mu^2)}$, compared to $f_{0n}^{(Q^2)}$, as can be seen in Table 1. The error curves in Figure 1 show the difference between moving the origin and calculating the effect of moving the origin from Eq. ?? when this is inserted in Eq. ?. Since single precision deliberately have been used the difference is in the 8th digit and occasional in the 7th as would be expected due to numerical noise from the finite numerical accuracy and the origin dependence in the length gauge for $f_{0n}^{(Q^2)}$ is therefore exact when disregarding numerical noise.

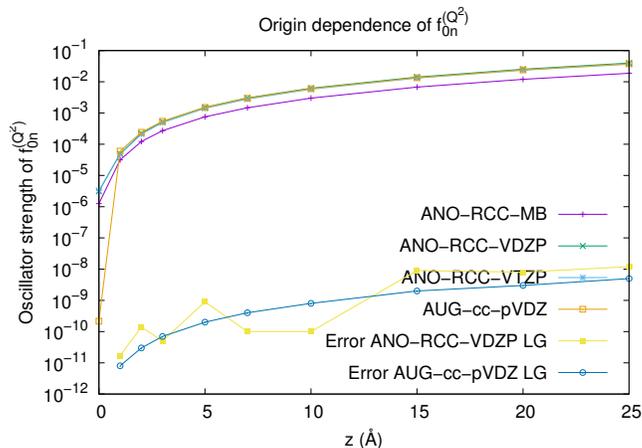


Figure 1: The origin dependence of $f_{0n}^{(Q^2)}$ in different basis sets. The error curves shows the numerical error in the origin dependence in the given basis set in the length gauge (LG) caused by numerical noise.

Despite the fact that the AUG-cc-pVDZ underestimates the $f_{0n}^{(Q^2)}$ contribution by four magnitudes the origin dependence of $f_{0n}^{(Q^2)}$ is very well behaved

Basis	$f_{0n}^{(\mu^2)}$	$f_{0n}^{(\mu^2)^p}$	R_{dip}	$f_{0n}^{(Q^2)}$	$f_{0n}^{(\mu O)}$	$f_{0n}^{(m^2)}$
ANO-RCC-MB	0.115	0.111	1.04	0.0125	-0.00588	
ANO-RCC-VDZP	0.295	0.286	1.03	0.0309	-0.0208	
ANO-RCC-VTZP	0.283	0.273	1.03	0.0327	-0.0196	
AUG-cc-pVDZ	0.281	0.168	1.68	$0.215 * 10^{-5}$	-0.583	$0.341 * 10^{-11}$

Table 1: The electric-dipole-electric-dipole ($f_{0n}^{(\mu^2)}$), in the length and velocity gauge, electric-quadrupole-electric-quadrupole ($f_{0n}^{(Q^2)}$), electric-dipole-electric-octupole ($f_{0n}^{(\mu O)}$), both in the length gauge, and magnetic-dipole-magnetic-dipole ($f_{0n}^{(m^2)}$), in the velocity gauge, intensities for the transition from the ground state to the third core-excited state in $[\text{FeCl}_4]^{1-}$ in different basis sets along with the ratio between the dipole intensities R_{dip} (see Eq. 28). All electric values have been multiplied by 10^4 and values below machine precision have been omitted.

which numerically demonstrates that the origin dependence is independent of the quality of the basis set.

The $f_{0n}^{(\mu O)}$ contribution also shows exact origin dependence, up to numerical rounding, for all basis sets as shown in Fig. 2. All contributions from $f_{0n}^{(\mu O)}$ are negative and gives a contribution that is only slightly smaller than $f_{0n}^{(Q^2)}$ in the ANO-RCC basis sets. In the AUG-cc-pVDZ basis set the $f_{0n}^{(\mu O)}$ contribution is very large which gives a total negative intensity for this transition, when truncating the oscillator strengths at the second order, as also reported earlier [1, 3]. By including the fourth order in the intensity the $f_{0n}^{(OO)}$ term should rectify the problem of total negative intensities provided that no other higher terms also grows disproportionately large. The convergence behaviour of the multipole expansion when summed as described in Eq. 11 is, however, not obvious in finite basis sets since the integrand is very sensitive to the choice of basis set [35].

3.3. Magnetic terms

Like the electric terms the magnetic terms also shows exact origin dependence in both the velocity and length gauge. Since the magnetic terms are not transformed in the mixed gauge, as shown in Section ??, the displacement of the origin independence in the mixed will therefore depend on both $f_{0n}^{(\mu^2)}$ and

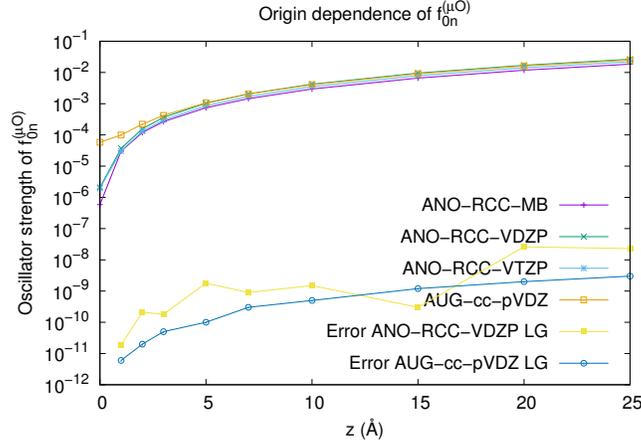


Figure 2: The origin dependence of $f_{0n}^{(\mu O)}$ in different basis sets. The error curves shows the numerical error in the origin dependence in the given basis set in the length gauge (LG) caused by numerical noise.

$f_{0n}^{(\mu^2)^p}$. Hence in the mixed gauge this will introduce an origin dependent error that will depend on the difference between $f_{0n}^{(\mu^2)^p}$ and $f_{0n}^{(\mu^2)}$

$$\Delta = f_{0n}^{(\mu^2)^p} - f_{0n}^{(\mu^2)} = f_{0n}^{(\mu^2)^p} \left(1 - \frac{f_{0n}^{(\mu^2)}}{f_{0n}^{(\mu^2)^p}}\right) = f_{0n}^{(\mu^2)^p} (1 - R_{dip}) \quad (28)$$

where the severity of the origin dependent error will depend on the size of $f_{0n}^{(\mu^2)^p}$ and the ratio R_{dip} , both shown in Table 1. For $f_{0n}^{(m^2)}$ the dependence on Δ will be quadratic as can be seen from Eq. ?? and Eq. ?. $f_{0n}^{(\mu^{\mathcal{M}})}$, in the mixed gauge, will also depend on the difference between the electric quadrupole in the velocity and length gauge.

Fig. 3 shows the origin dependence of the $f_{0n}^{(m^2)}$ contribution. The point where the origin of the coordinate system coincides with the Fe atom have been omitted to better show the origin dependence since the $f_{0n}^{(m^2)}$ contribution is negligible when the origin is placed on the Fe atom, as can be seen in Table 1.

In the velocity gauge the origin dependence of $f_{0n}^{(m^2)}$ is exact, down to numerical noise, as can be seen from the error curves labelled with VG in Fig. 3. In the mixed gauge, however, there is a strong dependence on the origin and ba-

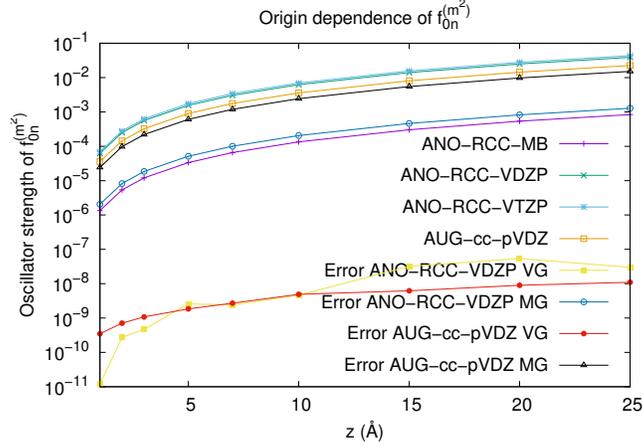


Figure 3: The origin dependence of $f_{0n}^{(m^2)}$ in both the velocity and mixed gauge in different basis sets. The error curves shows the numerical error in the origin dependence in the given basis set in the mixed gauge (MG) and velocity gauge (VG).

sis set as can be seen from by comparing the error curves in the AUG-cc-pVDZ and ANO-RCC-VDZP basis sets labelled with MG. In the ANO-RCC-VDZP error curve in the mixed gauge the difference is two orders of magnitude smaller than $f_{0n}^{(m^2)}$ while in the AUG-cc-pVDZ basis set the error is almost the same size as $f_{0n}^{(m^2)}$ which shows that if the origin is placed close to the Fe atom, less than 3 Å, the ANO-RCC-VDZP will, in this case, produce reliable results while AUG-cc-pVDZ basis set cannot. This observation is in line with the conclusions in [1] for the mixed gauge.

4. Conclusion

We have here discussed the problems that arises in finite basis sets from the mixed gauge often used or given as the length gauge in literature. We have here shown that the oscillator strengths from the multipole expansion also will be origin independent in the length gauge, but not in the mixed gauge, when the multipole expansion is truncated in the observable oscillator strength as demonstrated by Bernadotte et al.[2].

The consequences of not having the exact eigenfunctions and eigenvalues for \hat{H}_0 in perturbation theory have been discussed. We have shown that the usual approximations such as projecting the wave function on to a finite basis set and restricting the particle interaction usually used can be viewed as a way of constructing an approximate or effective zeroth order Hamiltonian \hat{H}'_0 and that this view can be favorable when deriving specific properties from a perturbation expansion. It is here shown that if the perturbation expansion does not depend on any intrinsic properties of \hat{H}_0 but only rely on \hat{H}_0 having a spectrum then any \hat{H}'_0 , which also have a spectrum, will also give the exact same perturbation expansion. Any conclusion or statement reached from the perturbation expansion for \hat{H}_0 will therefore also be valid for \hat{H}'_0 . Since \hat{H}'_0 per definition is always solved exactly the exact eigenfunctions and eigenvalues for \hat{H}'_0 are always known and since \hat{H}'_0 is the zeroth order Hamiltonian used the question about having the exact eigenfunctions and eigenvalues for the zeroth order Hamiltonian in perturbation theory is redundant since this is trivially fulfilled for \hat{H}'_0 .

Since Fermi's golden rule, which only require that \hat{H}_0 has a spectrum, is used in the derivation of the origin independent intensities [2] it is therefore trivial to show that this will hold for any approximate \hat{H}'_0 which also have a spectrum.

Even if the velocity gauge is the natural gauge from the perspective of minimal coupling the length gauge is equally valid also in finite basis sets since the origin independence of the intensities in both gauges always hold irrespectively of the choice of basis set and level of correlation. The erroneous conclusion that the length gauge is not origin independent is shown to stem from the usage of the hypervirial theorem to transform only the electric terms from the velocity to the length gauge while leaving the magnetic terms in velocity gauge. The resulting mixed gauge is shown to have an inter gauge dependence that will not be fulfilled in finite basis sets and therefore makes origin independence very basis set dependent.

Finally we have demonstrated the theoretical predictions numerically on the $[\text{FeCl}_4]^{1-}$ molecule. Here we have shown that the electric and magnetic con-

tributions to the oscillator strength shows exact origin dependence in both the length and velocity gauge. Since the exact origin independence of the oscillator strengths relies on exact cancellation then there will only be exact origin independence in finite basis sets if there is no inter gauge dependence for the cancellation. We have here demonstrated that even in reasonable basis sets the lack of origin independence in the mixed gauge, often used or presented as the length gauge in literature, can be very problematic when going beyond the dipole approximation.

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- [1] L. K. Sørensen, M. Guo, R. Lindh, M. Lundberg, Applications to metal K pre-edges of transition metal dimers illustrate the approximate origin independence for the intensities in the length representation, *Mol. Phys.* 115 (2017) 174.
- [2] S. Bernadotte, A. J. Atkins, C. R. Jacob, Origin-independent calculation of quadrupole intensities in X-ray spectroscopy, *J. Chem. Phys.* 137 (20) (2012) 204106.
- [3] P. J. Lestrange, F. Egidi, X. Li, The consequences of improperly describing oscillator strengths beyond the electric dipole approximation, *J. Chem. Phys.* 143 (2015) 234103.
- [4] P.-O. Löwdin, Studies in Perturbation Theory II. generalization of the Brillouin-Wigner Formalism III. solution of the Schrödinger Equation under a Variation of a Parameter, *J. Mol. Spectrosc.* 13 (1964) 326.

- [5] P.-O. Löwdin, Studies in Perturbation Theory IV. Solution of Eigenvalue Problem by Projection Operator Formalism, *J. Math. Phys.* 3 (1962) 969.
- [6] C. Møller, M. S. Plesset, Note on an Approximation Treatment for Many-Electron Systems, *Phys. Rev.* 46 (1934) 618.
- [7] C. Schwartz, Uses of Approximate Wave Functions, *Ann. Phys.* 2 (1959) 170.
- [8] I. Shavitt, Multi-state multireference rayleighschrödinger perturbation theory for mixed electronic states: Second and third order, *Int. J. Mol. Sci.* 3 (2002) 639.
- [9] S. T. Epstein, What is h_0 , in: C. H. Wilcox (Ed.), *Perturbation Theory and its Applications in Quantum Mechanics*, no. 16, John Wiley & Sons Inc, 1965, Ch. 3, p. 52.
- [10] R. F. Fink, Two new unitary-invariant and size-consistent perturbation theoretical approaches to the electron correlation energy, *Chem. Phys. Lett.* 428 (2006) 461.
- [11] J. H. V. Vleck, On σ -Type Doubling and Electron Spin in the Spectra of Diatomic Molecules, *Phys. Rev.* 33 (1929) 467.
- [12] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, J.-P. Malrieu, Introduction of n -electron valence states for multireference perturbation theory, *J. Chem. Phys.* 114 (2001) 10252.
- [13] I. Shavitt, L. T. Redmon, Quasidegenerate perturbation theories. A canonical van Vleck formalism and its relationship to other approaches, *J. Chem. Phys.* 73 (1980) 5711.
- [14] T. H. Schucan, H. A. Weidenmüller, The Effective Interaction in Nuclei and Its Perturbation Expansion : An Algebraic Approach, *Annals of Physics* 73 (1972) 108.

- [15] J. Olsen, O. Christiansen, H. Koch, P. Jørgensen, Surprising cases of divergent behavior in Møller-Plesset perturbation theory, *J. Chem. Phys.* 105 (1996) 5082.
- [16] R. K. Chaudhuri, J. P. Finley, K. F. Freed, Comparison of the perturbative convergence with multireference Møller-Plesset, Epstein-Nesbet, forced degenerate and optimized zeroth order partitionings: The excited BeH₂ surface, *J. Chem. Phys.* 106 (1997) 4067.
- [17] J. Olsen, M. P. Fülscher, On the convergence of multi-reference perturbation theory, *Chem. Phys. Lett.* 326 (2000) 225.
- [18] P.-O. Lowdin, The calculation of Upper and Lower Bounds of Energy Eigenvalues in Perturbation Theory by Means of Partitioning Techniques, in: C. H. Wilcox (Ed.), *Perturbation Theory and its Applications in Quantum Mechanics*, no. 16, John Wiley & Sons Inc, 1965, Ch. 12, p. 255.
- [19] J.-P. Malrieu, P. Durand, J. P. Duadey, Intermediate Hamiltonians as a new class of effective Hamiltonians, *J. Phys. A* 18 (1985) 809.
- [20] Y. G. Khait, M. R. Hoffmann, Explication and revision of generalized Van Vleck perturbation theory for molecular electronic structure, *J. Chem. Phys.* 117 (2002) 4133.
- [21] V. Hurtubise, K. F. Freed, The algebra of effective hamiltonians and operators: Exact operators, *Adv. Chem. Phys.* *LXXXIII* (1993) 465.
- [22] V. Hurtubise, K. F. Freed, The algebra of effective hamiltonians and operators: Truncated operators and computational aspects, *J. Chem. Phys.* 99 (1993) 7946.
- [23] B. Pradines, N. Suaud, J.-P. Malrieu, In Search of a Rational Dressing of Intermediate Effective Hamiltonians, *J. Phys. Chem. A* 119 (2015) 5207.
- [24] K. Andersson, P. Å. Malmqvist, B. O. Roos, A. J. Sadlej, K. Wolinski, 2nd-Order Perturbation Theory with a CASSCF Reference Function, *J. Phys. Chem.* 94 (1990) 5483.

- [25] K. Andersson, P. Å. Malmqvist, B. O. Roos, 2nd-Order Perturbation Theory with a Complete Active Space Self-Consistent Field Reference Function, *J. Chem. Phys.* 96 (1992) 1218.
- [26] B. Brandow, Linked-cluster expansions for the nuclear many-body problem., *Rev. Mod. Phys.* 39 (1967) 771.
- [27] G. Hose, U. Kaldor, Diagrammatic many-body perturbation theory for general model spaces., *J. Phys. B* 12 (1979) 3827.
- [28] D. J. Klein, Degenerate perturbation theory, *J. Chem. Phys.* 61 (1974) 786.
- [29] P.-O. Löwdin, The Historical Development of the Electron Correlation Problem, *Int. J. Quantum Chem.* 55 (1995) 77.
- [30] N. H. List, J. Kauczor, T. Saue, H. J. Aa. Jensen, P. Norman, Beyond the electric-dipole approximation: A formulation and implementation of molecular response theory for the description of absorption of electromagnetic field radiation, *J. Chem. Phys.* 142 (24) (2015) 244111.
- [31] N. H. List, T. Saue, P. Norman, Rotationally averaged linear absorption spectra beyond the electric-dipole approximation, *Mol. Phys.* 115 (2017) 63.
- [32] E. A. Hylleraas, Über den grundzustand des heliumatom., *Z. Phys.* 48 (1928) 469.
- [33] K. Nakayama, K. Hirao, R. Lindh, Different bases for different correlation effects: multireference Møller-Plesset perturbation theory in the extended basis function space, *Chem. Phys. Lett.* 300 (1999) 303.
- [34] S. Huzinaga, K. Hirao, Improved virtual orbitals in the extended basis function space, *J. Chem. Phys.* 66 (1977) 2157.
- [35] R. J. S. Crossley, The calculation of atomic transition probabilities, *Adv. At. Mol. Phys.* 5 (1969) 237.

- [36] J. C. Y. Chen, Off-diagonal hypervirial theorem and its applications, *J. Chem. Phys.* 40 (1964) 615.
- [37] F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. D. Vico, I. F. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. L. Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata, R. Lindh, MOLCAS 8: New Capabilities for Multiconfigurational Quantum Chemical Calculations across the Periodic Table, *J. Comp. Chem.* 37 (2016) 506.
- [38] T. E. Westre, P. Kennepohl, J. G. DeWitt, B. Hedman, K. O. Hodgson, E. I. Solomon, A Multiplet Analysis of Fe K-Edge $1s \rightarrow 3d$ Pre-Edge Features of Iron Complexes, *J. Am. Chem. Soc.* 119 (27) (1997) 6297.
- [39] M. Guo, L. K. Sørensen, M. G. Delcey, R. V. Pinjari, M. Lundberg, Simulations of iron K pre-edge X-ray absorption spectra using the restricted active space method, *Phys. Chem. Chem. Phys.* 18 (2016) 3250.
- [40] B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, New Relativistic ANO Basis Sets for Transition Metal Atoms, *J. Chem. Phys.* 109 (2005) 6575.
- [41] B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, New Relativistic ANO Basis Sets for Transition Metal Atoms, *J. Phys. Chem. A* 108 (2004) 2851.
- [42] D. E. Woon, T. H. Dunning, Jr, Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon, *J. Chem. Phys.* 98 (1993) 1358.
- [43] N. Balabanov, K. Peterson, Basis set limit electronic excitation energies, ionization potentials, and electron affinities for the $3d$ transition metal

atoms: Coupled cluster and multireference methods, *J. Chem. Phys.* 125 (2006) 074110.

- [44] P.-Å. Malmqvist, B. O. Roos, *Chem. Phys. Lett.* 155 (2) (1989) 189.
- [45] P. Å. Malmqvist, B. O. Roos, B. Schimmelpfennig, The restricted active space (RAS) state interaction approach with spin-orbit coupling, *Chem. Phys. Lett.* 357 (2002) 230.
- [46] M. Douglas, N. M. Kroll, Quantum Electrodynamical corrections to the structure of Helium, *Ann. Phys.* 82 (1974) 89.
- [47] B. A. Heß, Relativistic electronic-structure calculations employing a two-component no-pair formalism with external field projection operators, *Phys. Rev. A* 33 (1986) 3742.