What do we approximate and what are the consequences in perturbation theory?

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We present a discussion of the consequences in perturbation theory when an exact eigenfunctions and eigenvalues to the zeroth order Hamiltonian $H_0$ cannot be found. Since the usual approximations such as projecting the wavefunction on to a finite basis set and restricting the particle interaction is a way of constructing an approximate zeroth order Hamiltonian $H'_0$ we will here argue that the exact eigenfunctions and eigenvalues are always found for $H'_0$. We will show that as long as the perturbative expansion does not depend on any intrinsic properties of $H_0$ but only on knowing the exact eigenfunctions and eigenvalues then any perturbative statement, such as origin independence intensities, will be true for any $H'_0$ provided that $H'_0$ has a spectrum. We will use this to show that the origin independence for the intensities is trivially fulfilled in the velocity gauge but also can be fulfilled exactly in the length gauge if an appropriate $H'_0$ is chosen. Finally a small numerically demonstration of the origin dependence of the terms for the second-order intensities in both the length and velocity gauge is undertaking to numerically illustrate the theoretical statements.

Keywords: Perturbation theory, Approximate methods, Oscillator Strengths, Quadrupole intensities, Properties, X-ray Spectroscopy

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I. INTRODUCTION

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 $[1,2]$. 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 Möller-Plesset perturbation theory $[3]$, since the SCF equations are solved in a finite basis set. When the exact eigenfunctions $\hat{H}_0$ cannot be found then in most textbooks it is stated that an approximate wavefunction to $\hat{H}_0$ is found. The consequences of not having the exact eigenfunctions and eigenvalues of $\hat{H}_0$ are rarely discussed if at all $[4]$. When the focus is on $\hat{H}_0$ the aim is to construct a better $\hat{H}_0 \, [5, 6]$ and not on whether or not 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 $[3, 7, 8]$, their relations $[9]$, the convergence $[10]$ or lack thereof $[11, 13]$, bound for the energies $[14]$, eliminating of intruder states $[15, 16]$, conceptional developments of effective Hamiltonians $[17, 19]$, multiconfigurational $[20, 21]$ or degenerate perturbation theory $[22, 24]$ 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 $[25]$.

We will here show that the exact eigenfunctions and eigenvalues are always found but that these need not be for the exact $\hat{H}_0$ but for some approximate or effective zeroth order Hamiltonian $\hat{H}_0'$. 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 $[26]$, 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 $[26]$ always hold in the velocity gauge but not in length gauge. It will be shown that the problems in the length gauge stems from not having the exact same commutation relations for $\hat{H}_0$ and $\hat{H}_0'$ when transforming from the velocity to the length gauge. 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 $[26]$ for $[\text{FeCl}_4]^-$ in the velocity and length gauge $[27]$.

II. 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. We will here give an example from Configuration-Interaction (CI) theory $[28]$ on how a series of approximate Hamiltonians can be constructed from the exact solution.

Thereafter we will show that the error in approximate calculations when transforming from the velocity gauge to the length gauge stems from the assumed non-exact commutation relation between $\hat{H}_0'$ and $\hat{r}$ and not from non-exact eigenfunctions of $\hat{H}_0$. Finally we will use the findings from the construction of approximate Hamiltonians to to show that the so-called quadrupole intensities, recently derived by Bernadotte et al. $[26]$, will be origin independent in the velocity 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, illustrate where $\hat{H}_0'$ enters and the difference between the length and velocity gauge and otherwise refer to the excellent paper by Bernadotte et al. $[26]$ for complete derivations.

A. 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 $\hat{U}$

$$\hat{H}' = \hat{H}_0' + \hat{U},$$  \hspace{1cm} (2)$$

where again it is assumed that the exact eigenfunctions and eigenvalues for $\hat{H}_0'$ is known, is also acceptable. Whether $\hat{H}_0$ or $\hat{H}_0'$ is used it will later be shown that the exact same derivation for the oscillator strengths, in the velocity representation, in Sec. II D could be performed and exactly the same conclusion with respect to the origin independence would be reached. In fact 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 $\hat{H}_0$, provided that $\hat{H}_0$ and $\hat{H}_0'$ has a spectrum. If, however, the perturbation treatment depend on some intrinsic property of $\hat{H}_0$ the perturbation expansions will then only be identical for another $\hat{H}_0'$ 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. We will here limit ourselves to perturbation expansions which does not depend on any intrinsic properties of $\hat{H}_0$ and hence the choice of $\hat{H}_0$, and consequently $\hat{H}$, can be chosen independently of $\hat{U}$. One is in fact free to choose almost anything as $\hat{H}_0$ and $\hat{U}$, even to include some fictitious interaction,

$$\hat{H} = \hat{H}_0 - \hat{H}_{fic} + \hat{H}_0 + \hat{H}_{fic} = \hat{H}_0 + \hat{U}$$ \hspace{1cm} (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 [3] where the perturbation operator $\hat{\Phi}$, known as the fluctuation operator,

$$\hat{\Phi} = \hat{H} - \hat{f} - h_{nuc}$$ \hspace{1cm} (4)$$

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

### B. 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 and etc. 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

$$\hat{H}_0 = \hat{H}_0 - \hat{H}_{fic} + \hat{H}_0 + \hat{H}_{fic} = \hat{H}_0 + \hat{U}$$ \hspace{1cm} (5)$$

where the remaining effects from the finite basis and incomplete correlation treatment is 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. 4 is, however, still allowed. In practice it is therefore the approximate zeroth order Hamiltonian $\hat{H}_0'$ that will be solved and not $\hat{H}_0$. Hence it is therefore not the exact Hamiltonian $\hat{H}$ in Eq. 1 that is being solved but the alternative approximate or effective Hamiltonian $\hat{H}'$ in Eq. 2 when a perturbation is applied to the system. Any perturbative derivation and conclusions should therefore be based on $\hat{H}_0'$ and not $\hat{H}_0$.

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. We here note that what is called the exact Hamiltonian here is in fact arbitrary which is in line with all current theories in physics where any Hamiltonian is an effective theory dependent Hamiltonian. $\hat{H}_0'$ in Eq. 5 therefore contain the approximate or fictive interaction introduced in Eq. 3.

The approximate Hamiltonian $\hat{H}_0'$ can then be perturbed with $\hat{U}$ as shown in Eq. 2 in order to find a perturbative solution to $\hat{H}'$. Since the exact eigenfunctions to $\hat{H}_0'$ will always be found by construction, disregarding convergence and rounding errors along with other numerical problems, and all effects of the finite basis and incomplete correlation treatment is in $\hat{H}_{rest}$ then any conclusions based on the perturbative treatment therefore does not depend on the size of the basis set or the level of correlation treatment.
An example of creating several levels of approximate Hamiltonians can be seen going from the FCI solution in a complete basis, which we will here take as the exact solution, to a truncated CI expansion in a finite basis. In this case we can write down the CI-matrix or Hamiltonian in the given basis. The CI-matrix \( H_0 \)

\[
H_0 C = EC
\]

multiplied with the CI-vector \( C \) gives the energy \( E \) where the CI-vector \( C \)

\[
|C\rangle = \sum_i C_i|i\rangle
\]

contains the coefficients \( C_i \) for the linear expansion in the Slater determinants \( |i\rangle \).

If the Slater determinants in the FCI expansion are constructed directly from the basis functions and the finite basis set form a true subset of the complete basis set then the Slater determinants, in the finite basis, will not change when the basis is reduced from the complete basis to the finite basis. Reducing to a finite basis set will then be equivalent to restricting the number of Slater determinants in Eq. 7 to a finite number \( m \), where all determinants only containing the basis functions of the finite basis have been included,

\[
|C'\rangle = \sum_i^{m} C_i'|i\rangle
\]

and generating a new set of CI-coefficients \( C' \). The approximate CI-matrix \( H'_0 \) can easily be separated from the exact CI-matrix \( H_0 \), since matrix multiplication is distributive,

\[ H_0 = H'_0 + H_0 - H'_0 = H'_0 + H_{\text{rest}} \]

with a remaining part \( H_{\text{rest}} \). \( H'_0 \) is now FCI in a finite basis. The dimension of \( H'_0 \) is smaller than that of \( H_0 \) and therefore \( H'_0 \) will only contain approximations to certain solutions in \( H_0 \). Furthermore not only will the CI-coefficients change going from a complete basis to a finite basis but also the matrix elements in \( H'_0 \) will also differ from those in \( H_0 \) and hence \( H_{\text{rest}} \) will therefore also be non-zero in the parts where \( H'_0 \) have been subtracted.

If a suitable orbital rotation of the primitive basis in Eq. 8 is performed then the FCI solution in the finite basis can be reduced to the regular CISD solution in the same basis. We here note that the FCI solution is invariant to all orbital rotations but the CISD is not. Arranging the CI-vector \( C \) in Eq. 8 according to the regular CI hierarchy the FCI CI-matrix, in the rotated basis, can be written

\[
H'_0 = \sum_{i,j=0}^{N} \langle i|H'_0|j\rangle
\]

where the sum over \( i, j \) is over all excitation levels in the CI hierarchy from zero to \( N \). Truncating the CI-expansion at the CISD level the Hamiltonian \( H'_0 \) can be written as

\[
H''_0 = \sum_{i,j=0}^{N} \langle i|H'_0|j\rangle - \sum_{i=0,j=3}^{N} \langle i|H'_0|j\rangle - \sum_{i=3,j=0}^{N} \langle i|H'_0|j\rangle = \sum_{i,j=0}^{2} \langle i|H'_0|j\rangle.
\]

Solving the CISD equations with the Hamiltonian in Eq. 11 will give the exact eigenfunctions and eigenvalues for \( H'_0 \) which will approximate some solutions in \( H_0 \).

When an external perturbation is applied to the zeroth order Hamiltonian then it is not applied to the exact Hamiltonian \( H_0 \) but to some approximative Hamiltonian \( H'_0 \) or \( H''_0 \). Since the exact eigenfunctions for \( H'_0 \) or \( H''_0 \) are trivially known the discussion about having exact eigenfunctions and eigenvalues for the zeroth order Hamiltonian in perturbation theory is redundant.

C. The length and velocity gauge

When approximating \( \hat{H}_0 \) by \( \hat{H}'_0 \) the gauge invariance may be affected since commutation relations with \( \hat{H}'_0 \) may be slightly different for those for \( \hat{H}_0 \). Since the implementation of the quadrupole intensities used here is in length gauge the conversion from the velocity to the length gauge, where \( \hat{p} \) is substituted with \( r \), is central in showing how
origin independence of the quadrupole intensities does not hold, in usual quantum chemistry calculations, in both
gauges when \( H_0 \) is approximated by \( H'_0 \).

Using the Hamiltonian for the Schrödinger equation of a molecular system in the Born-Oppenheimer approximation
in Eq. (21) the following commutation relations are known [26]

\[
[r_{i,\alpha}, \hat{H}_0] = \frac{i\hbar}{m} \hat{p}_{i,\alpha},
\]

(12)

\[
[r_{i,\alpha}r_{i,\beta}, \hat{H}_0] = \frac{i\hbar}{m}(\hat{p}_{i,\alpha}r_{i,\beta} + r_{i,\alpha}\hat{p}_{i,\beta})
\]

(13)

\[
[r_{i,\alpha}r_{i,\beta}r_{i,\gamma}, \hat{H}_0] = \frac{i\hbar}{m}(\hat{p}_{i,\alpha}r_{i,\beta}r_{i,\gamma} + r_{i,\alpha}\hat{p}_{i,\beta}r_{i,\gamma} + r_{i,\alpha}r_{i,\beta}\hat{p}_{i,\gamma})
\]

(14)

while other choices of Hamiltonian may not show the same commutation relations. By using the commutations
relations the different electric terms in the multipole expansion can be converted from the velocity to the length
representation

\[
\langle 0 | \hat{\mu}_\alpha^p | n \rangle = -i \frac{E_{0n}}{\hbar} \langle 0 | \hat{\mu}_\alpha | n \rangle
\]

(15)

\[
\langle 0 | \hat{Q}_{\alpha\beta}^p | n \rangle = -i \frac{E_{0n}}{\hbar} \langle 0 | \hat{Q}_{\alpha\beta} | n \rangle
\]

(16)

\[
\langle 0 | \hat{Q}_{\alpha\alpha\beta}^\mu | n \rangle = -i \frac{E_{0n}}{\hbar} \langle 0 | \hat{Q}_{\alpha\alpha\beta} | n \rangle.
\]

(17)

The requirement for exact conversion from the velocity to the length representation is usually stated as having the
exact eigenfunctions for \( \hat{H}_0 \). In Sec. [11] it was demonstrated that obtaining the exact zeroth eigenfunctions is trivial.
This, however, does not mean that the conversion from the velocity to the length representation is always exact. Since
\( \hat{H}_0 \) in Eq. (21) has never been solved exactly for \( N > 2 \), for which the commutations relations in Eqs. (12,14) is based
upon, but only approximate Hamiltonians \( \hat{H}'_0, \hat{H}''_0, \ldots \) of \( \hat{H}_0 \) have been solved. This means that the commutation
relations in Eqs. (12,14) should not be based on \( \hat{H}_0 \) but on an approximative Hamiltonian \( \hat{H}'_0 \)

\[
[r_{i,\alpha}, \hat{H}'_0] \cong \frac{i\hbar}{m} \hat{p}_{i,\alpha},
\]

(18)

\[
[r_{i,\alpha}r_{i,\beta}, \hat{H}'_0] \cong \frac{i\hbar}{m}(\hat{p}_{i,\alpha}r_{i,\beta} + r_{i,\alpha}\hat{p}_{i,\beta})
\]

(19)

\[
[r_{i,\alpha}r_{i,\beta}r_{i,\gamma}, \hat{H}'_0] \cong \frac{i\hbar}{m}(\hat{p}_{i,\alpha}r_{i,\beta}r_{i,\gamma} + r_{i,\alpha}\hat{p}_{i,\beta}r_{i,\gamma} + r_{i,\alpha}r_{i,\beta}\hat{p}_{i,\gamma}).
\]

(20)

The commutation relations in Eqs. (18,20) shows that the conversion from the velocity to the length representation
depends on the commutation relations in Eqs. (18,20) and not on having the exact eigenfunctions and eigenvalues
for \( \hat{H}'_0 \). If the commutation relations in Eqs. (18,20) become exact the conversion from the velocity to the length
representation exact otherwise it will only be approximate which we in Sec. [III] will use to demonstrate numerically
that exact origin independence is only found in the velocity gauge in the approximate calculations performed in
quantum chemistry. Even if the commutation relations in Eqs. (18,20) are exact there is, however, no guarantee that
\( \hat{H}'_0 \) will be equal to \( \hat{H}_0 \) [29].

D. Origin independence of the oscillator strengths

We will in this section try to recapitulate the ideas and derivations of Bernadotte et al. [26] to show how \( \hat{H}'_0 \) enters
and the effects of this along with the points illustrated in the applications in Sec. [III] For complete derivations of this
topic we refer to Bernadotte et al. [26].

It is thought 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

\[
\hat{H}_0 = \sum_{i=1}^{N} \frac{\hat{p}_{i}^2}{2m_e} + V(r_1, \ldots, r_N)
\]

(21)
where \( \hat{U}(t) \) is the time-dependent perturbation

\[
\hat{U}(t) = \frac{e A_0}{2m_e c} \sum_i \exp(i(k \cdot r_i - \omega t))(\mathcal{E} \cdot \hat{p}_i)
\]  

(22)

from a monochromatic linearly polarized electromagnetic wave. In Eq. (22) \( k \) is the wave vector pointing in the direction of propagation, \( \mathcal{E} \) the polarization vector perpendicular to \( k \) and \( \omega \) is the angular frequency.

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

\[
\omega = \omega_{0n} = \frac{E_n - E_0}{\hbar}
\]

(23)

the explicit time dependence can be eliminated from the transition rate

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

(24)

Where in Eq. (24) the transition moments \( T_{0n} \) have been introduced. The effect of the weak electromagnetic field can now be expressed as a time-independent expectation value.

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. (4) 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 and level of correlation.

This can also be demonstrated numerically since exact origin dependence, in the velocity representation, should only be observed for FCI in a complete basis if the exact eigenfunctions for \( \hat{H}_0 \) in Eq. (21) was required and deviations from exact origin dependence should be observed in approximate calculations. We, as expected, always see exact origin independence regardless of basis and correlation level in the velocity gauge. Several numerical examples of the exact origin dependence will be given in Sec. III for [FeCl4]1− in different basis sets at the RASSCF level of correlation.

Bernadotte et al. showed that origin independence in the oscillator strengths \( f_{0n} \)

\[
f_{0n} = \frac{2m_e}{e^2 E_{0n}} |T_{0n}|^2,
\]

(25)

where \( E_{0n} = E_n - E_0 \) is the difference in the eigenstates of the unperturbed molecule, comes naturally provided that the collection of the terms in Taylor expansion of the exponential of the wave vector \( k \) in Eq. (22) is collected to the same order in the observable oscillator strengths in Eq. (26)

\[
f_{0n} = f_{0n}^{(0)} + f_{0n}^{(1)} + f_{0n}^{(2)} + \ldots = \frac{2m_e}{e^2 E_{0n}} |T_{0n}^{(0)} + T_{0n}^{(1)} + T_{0n}^{(2)} + \ldots|^2
\]

(26)

and not in the transition moments \( T_{0n} \) traditionally done.

1. Isotropically averaged oscillator strengths

Truncating the expansion of the oscillator strengths in Eq. (26) at the second order gives the dipole and the quadrupole intensities. The zeroth order in Eq. (26) is the electric-dipole-electric-dipole \( f_{0n}^{(1)} \) contribution

\[
\langle f_{0n}^{(1)} \rangle_{iso} = \frac{2m_e}{3c^2 \hbar^2} E_{0n} \sum_\alpha \langle 0 | \hat{\mu}_\alpha | n \rangle^2 = \frac{2m_e}{3c^2 \hbar^2} E_{0n} \langle 0 | \hat{\mu} | n \rangle^2
\]

(27)

where the sum is over \( x, y, z \) if Cartesian coordinates is used. The first order \( f_{0n}^{(1)} \) in Eq. (26) vanishes while the second order \( f_{0n}^{(2)} \) gives four non-zero contributions. The electric-quadrupole-electric-quadrupole \( f_{0n}^{(2)} \)

\[
\langle f_{0n}^{(2)} \rangle_{iso} = \frac{m_e}{20c^2 \hbar^4 c^2} E_{0n}^3 \left[ \sum_\alpha \langle 0 | \hat{Q}_{\alpha\beta} | n \rangle^2 - \frac{1}{3} \sum_\alpha \langle 0 | \hat{Q}_{\alpha\alpha} | n \rangle^2 \right],
\]

(28)
the magnetic-dipole-magnetic-dipole \( f^{(m^2)}_{0n} \)

\[
\langle f^{(m^2)}_{0n} \rangle_{iso} = \frac{2m_e}{3e^2\hbar^2} E_{0n} \sum_{\alpha} \langle 0 | \hat{m}_{\alpha} | n \rangle^2 = \frac{2m_e}{3e^2\hbar^2} E_{0n} \langle 0 | \hat{m} | n \rangle^2,
\]

(29)

the electric-dipole-electric-octupole \( f^{(\mu O)}_{0n} \)

\[
\langle f^{(\mu O)}_{0n} \rangle_{iso} = -\frac{2m_e}{45e^2\hbar^4 c^2} E_{0n}^3 \sum_{\alpha\beta} \langle 0 | \hat{\mu}_{\beta} | n \rangle \langle 0 | \hat{O}_{\alpha\beta} | n \rangle,
\]

(30)

and the electric-dipole-magnetic-quadrupole \( f^{(\mu M)}_{0n} \) contributions

\[
\langle f^{(\mu M)}_{0n} \rangle_{iso} = \frac{m_e}{3e^2\hbar^3 c} E_{0n}^2 \sum_{\alpha\beta\gamma} \varepsilon_{\alpha\beta\gamma} \langle 0 | \hat{\mu}_{\beta} | n \rangle Im \langle 0 | \hat{M}_{\gamma\alpha} | n \rangle
\]

(31)

which all have to be included to obtain origin independence.

2. Origin dependence of the transition moments

As shown in \[26\] the individual terms in the expansion of the oscillator strengths in Eqs. \[28,31\] are not individually origin independent but rely on exact cancellation for the total oscillator strength order by order. The proof of the exact cancellation after the multipole expansion is more complicated than that for the exact expression repeated in Appendix A and we will therefore refer to Bernadotte et al. \[26\] for the proof. When the origin is shifted from \( O \) to \( O + a \), in the velocity gauge, the electric-quadrupole transition moments

\[
\langle 0 | \hat{Q}_{\alpha\beta}^{(p)} (O + a) | n \rangle = \langle 0 | \hat{Q}_{\alpha\beta}^{(p)} (O) | n \rangle - a_{\beta} \langle 0 | \hat{\mu}_{\alpha} | n \rangle - a_{\alpha} \langle 0 | \hat{\mu}_{\beta} | n \rangle,
\]

(32)

where the \( \alpha, \beta \) are the different \( x, y, z \) components, the electric-octupole transition moments

\[
\langle 0 | \hat{O}_{\alpha\beta\gamma}^{(p)} (O + a) | n \rangle = \langle 0 | \hat{O}_{\alpha\beta\gamma}^{(p)} (O) | n \rangle - a_{\gamma} \langle 0 | \hat{Q}_{\alpha\beta}^{(p)} (O) | n \rangle - a_{\alpha} \langle 0 | \hat{Q}_{\beta\gamma}^{(p)} (O) | n \rangle + a_{\alpha} a_{\gamma} \langle 0 | \hat{\mu}_{\beta} | n \rangle + a_{\beta} a_{\gamma} \langle 0 | \hat{\mu}_{\alpha} | n \rangle,
\]

(33)

the magnetic-dipole transition moments

\[
\langle 0 | \hat{m}_{\alpha} (O + a) | n \rangle = \langle 0 | \hat{m}_{\alpha} (O) | n \rangle - \varepsilon_{\alpha\beta\gamma} \frac{1}{2c} \langle 0 | \hat{\mu}_{\gamma} | n \rangle
\]

\[
\cong \langle 0 | \hat{m}_{\alpha} (O) | n \rangle - \varepsilon_{\alpha\beta\gamma} \frac{iE_{0n}}{2\hbar c} \langle 0 | \hat{\mu}_{\gamma} | n \rangle,
\]

(34)

where \( \varepsilon_{\alpha\beta\gamma} \) is the Levi-Civita tensor, and the magnetic-quadrupole transition moments

\[
\langle 0 | \hat{M}_{\gamma\alpha} (O + a) | n \rangle = \langle 0 | \hat{M}_{\gamma\alpha} (O) | n \rangle
\]

\[
- \frac{1}{3c} \varepsilon_{\alpha\beta\gamma} a_{\gamma} \langle 0 | \hat{Q}_{\beta\delta}^{(p)} (O) | n \rangle + \frac{2}{3c} \varepsilon_{\alpha\beta\gamma} a_{\beta} a_{\gamma} \langle 0 | \hat{\mu}_{\delta} | n \rangle
\]

\[
+ \frac{2}{3} \delta_{\alpha\beta} \langle a \cdot (0 | \hat{m} (O) | n \rangle - 2a_{\beta} \langle 0 | \hat{m}_{\alpha} (O) | n \rangle
\]

\[
\cong \langle 0 | \hat{M}_{\gamma\alpha} (O) | n \rangle
\]

\[
+ \frac{iE_{0n}}{3\hbar c} \varepsilon_{\alpha\beta\gamma} a_{\gamma} \langle 0 | \hat{Q}_{\beta\delta}^{(p)} (O) | n \rangle - \frac{i2E_{0n}}{3\hbar c} \varepsilon_{\alpha\beta\gamma} a_{\beta} a_{\gamma} \langle 0 | \hat{\mu}_{\delta} | n \rangle
\]

\[
+ \frac{2}{3} \delta_{\alpha\beta} \langle a \cdot (0 | \hat{m} (O) | n \rangle - 2a_{\beta} \langle 0 | \hat{m}_{\alpha} (O) | n \rangle
\]

(35)

all produce all lower order contributions which are all in the velocity gauge. In the magnetic terms in Eqs. \[33,34\] and the \( \hat{\mu}_{\delta}^{(p)} \) and \( \hat{Q}_{\beta\delta}^{(p)} \) terms have been transformed from the velocity to the length gauge as described in Sec. II A. We here note that the energy appearing in the transformation from the velocity to the length gauge is calculated exactly
for \( \hat{H}'_0 \) and the error is therefore only from the commutation relations in Eqs. 18-20. Transforming the electric terms in Eqs. 32 and 33 from the velocity to the length gauge

\[
\langle 0 | \hat{Q}_{\alpha \beta}(O + a) | n \rangle = \langle 0 | \hat{Q}_{\alpha \beta}(O) | n \rangle - a_{\beta} \langle 0 | \hat{\mu}_{\alpha} | n \rangle - a_{\alpha} \langle 0 | \hat{\mu}_{\beta} | n \rangle
\]

(36)

and

\[
\langle 0 | \hat{Q}_{\alpha \beta}(O + a) | n \rangle = \langle 0 | \hat{Q}_{\alpha \beta}(O) | n \rangle - a_{\gamma} \langle 0 | \hat{Q}_{\alpha \gamma}(O) | n \rangle - a_{\alpha} \langle 0 | \hat{Q}_{\beta \gamma}(O) | n \rangle + a_{\alpha} a_{\beta} \langle 0 | \hat{\mu}_{\gamma} | n \rangle + a_{\alpha} a_{\gamma} \langle 0 | \hat{\mu}_{\beta} | n \rangle + a_{\beta} a_{\gamma} \langle 0 | \hat{\mu}_{\alpha} | n \rangle
\]

(37)

only produce lower order terms in the length gauge.

The conversion from velocity to length gauge is, however, only exact if the commutation relations in Sec. II C are exact. If the commutations relations in Sec. II C are not exact the magnetic-dipole and magnetic-quadrupole transition moments will not show exact origin dependence in the length representation and hence the origin independence of the total oscillator strengths will not be conserved. We here note that the magnetic terms in the multipole expansion is not transformed when going from the velocity to the length gauge.

In the perturbative inclusion of the electromagnetic fields it is, as always, assumed that the exact eigenfunctions to \( \hat{H}_0 \) is known. If an approximate wavefunction to \( \hat{H}_0 \) is used the origin dependence of the various second order oscillator strengths contributions in Eqs. 32-35 need no longer be exact and hence origin independence is no longer guaranteed since the origin independence of the oscillator strengths rely on exact cancellation. With the above interpretation, which is the prevalent interpretation, the perturbative requirement is therefore only exactly fulfilled for full configuration interaction (FCI) in a complete basis.

We will, however, show that the the requirement for having the exact eigenfunctions is trivially fulfilled and using the velocity representation will automatically insure origin independence, if all terms for a given order in the oscillator strengths contributions in Eqs. 32-35 need no longer be exact and hence origin independence is no longer guaranteed since the origin independence of the oscillator strengths rely on exact cancellation. With the above interpretation, which is the prevalent interpretation, the perturbative requirement is therefore only exactly fulfilled for full configuration interaction (FCI) in a complete basis.

We will, however, show that the the requirement for having the exact eigenfunctions is trivially fulfilled and using the velocity representation will automatically insure origin independence, if all terms for a given order in the oscillator strengths in Eqs. 18-20 are kept, while using the length representation will depend on how exact the commutation relations in Eqs. 18-20 are.

### III. APPLICATION

To numerically prove the exact origin independence in the velocity gauge for any basis set or level of correlation we will use the recently implemented origin independent quadrupole intensites \[27\] part in MOLCAS \[30\]. Since our implementation is in the length gauge and 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 \[20\]. However, since the origin independence relies on exact cancellation it is sufficient to show the exact origin dependence of the different terms in Eqs. 32-35 in the velocity gauge for the \([\text{FeCl}_4]^{-}\) molecule using different basis sets and level of correlation. In the length gauge the exact origin dependence is only found for the electric terms and not for the magnetic terms as can be seen from Eqs. 34-37

#### A. Computational details

We have choosen the \([\text{FeCl}_4]^{-}\) molecule due to its significant increase in pre-edge intensity, through 4p mixing, in X-ray absorption spectroscopy (XAS) \[34, 35\]. The 4p mixing gives rise to very large \( f_{\text{on}}^{(\mu^2)} \) and hence makes the terms in Eqs. 32-35 grow significantly faster and thereby making the conservation of origin independence more difficult \[27\].

We have thought used the ANO-RCC basis sets since these basis sets have been shown to perform reasonbably well in conserving the origin independence in the length representation for the quadrupole intensities \[27\]. Furthermore we have included AUG-cc-pVDZ basis set, which in a previous application on \([\text{FeCl}_4]^{-}\) gave unphysical results, to show that good basis sets are not needed to have exact origin independence in the velocity gauge but that the length 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 \([\text{FeCl}_4]^{-}\) 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 \[36, 37\] which uses a biorthonormalization procedure which removes the gauge dependence of non-orthogonarl states.

While the Hamiltonian used in the derivation of the intensities in Sec. II D is based on the Schrödinger equation we will use a second-order Douglas-Kroll-Hess Hamiltonian \[38, 39\] to take into account the scalar relativistic effects, however, as shown in Sec. II B 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 velocity and not in the length gauge we will try to vary the basis set to illustrate the point that the perturbation does depend on the choice of $H_0$, as stated in Sec. [13] and that the in the length gauge the electric terms will show exact origin dependence but the magnetic terms will not. We will therefore show the exact origin dependence of the electric terms in the length gauge along with the exact origin dependence of $f_{0n}^{(m^2)}$ in the velocity gauge and the basis set dependence in the length gauge.

B. Electric terms

As shown in Eq. [36] the origin dependence of the electric-quadrupole transition moments 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. $f_{0n}^{(Q^2)}$ 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 I. The error curves in Figure 1 show the difference between moving the origin and calculating the effect of moving the origin from Eq. [36]. Since single precision 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 accuracy and the origin dependence in the length gauge for $f_{0n}^{(Q^2)}$ is therefore exact when disregarding numerical noise.

![Origin dependence of $f_{0n}^{(Q^2)}$](image)

**FIG. 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 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 as also reported earlier [27, 33]. 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 disproportionatly large. The convergence behaviour of the multipole expansion is, however, not obvious.
TABLE I. The electric-dipole-electric-dipole \( f_{\mu}^{(\mu^2)} \), in the length and velocity gauge, electric-quadrupole-electric-quadrupole \( f_{\mu}^{(Q^2)} \), electric-dipole-electric-octupole \( f_{\mu}^{(\mu O)} \), both in the length gauge, and magnetic-dipole-magnetic-dipole \( f_{\mu}^{(m^2)} \), same in both gauges, intensities for the transition from the ground state to the third core-excited state in \([\text{FeCl}_4]^{-}\) in different basis sets along with the ratio between the dipole intensities \( R_{\text{dip}} \). All values have been multiplied by \( 10^4 \) and values below \( 10^{-19} \) have been omitted.

\[
\begin{array}{ccccccc}
\text{Basis} & f_{\mu}^{(\mu^2)} & f_{\mu}^{(Q^2)} & f_{\mu}^{(\mu O)} & f_{\mu}^{(m^2)} & f_{\mu}^{(m^2)} & R_{\text{dip}} \\
\text{ANO-RCC-MB} & 0.115 & 0.111 & 1.04 & 0.0125 & 0.00588 & 0.347 \\
\text{ANO-RCC-VDZP} & 0.295 & 0.286 & 1.03 & 0.0309 & 0.0208 & 0 \\
\text{ANO-RCC-VTZP} & 0.283 & 0.273 & 1.03 & 0.0327 & 0.0196 & 0 \\
\text{AUG-cc-pVDZ} & 0.281 & 0.168 & 1.68 & 0.215 & 0.341 & 0 \\
\end{array}
\]

FIG. 2. The origin dependence of \( f_{\mu}^{(\mu O)} \) 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.

C. Magnetic terms

While all the electric terms shows exact origin dependence in both the velocity and length gauge the same is not true for the magnetic terms. Since the magnetic terms are not transformed when changing from the velocity to the length gauge the displacement of the origin will therefore depend on \( f_{\mu}^{(\mu^2)} \) in both gauges. Hence in the length gauge this will introduce an error that will depend on the difference between \( f_{\mu}^{(\mu^2)} \) and \( f_{\mu}^{(\mu^2)} \)

\[
\Delta = f_{\mu}^{(\mu^2)} - f_{\mu}^{(\mu^2)} = f_{\mu}^{(\mu^2)} (1 - f_{\mu}^{(\mu^2)} f_{\mu}^{(\mu^2)}) = f_{\mu}^{(\mu^2)} (1 - R_{\text{dip}})
\]

where the severity of the error will depend on the size of \( f_{\mu}^{(\mu^2)} \) and the ratio \( R_{\text{dip}} \), both shown in Table I. For \( f_{\mu}^{(m^2)} \) the dependence on \( \Delta \) will be quadratic as can be seen from Eq. 29 and Eq. 34.

Fig. 3 shows the origin dependence of the \( f_{\mu}^{(m^2)} \) 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 \( f_{\mu}^{(m^2)} \) contribution is negligible when the origin is placed on the Fe atom, as can be seen in Table I.

In the velocity gauge the origin dependence of \( f_{\mu}^{(m^2)} \) is exact, down to numerical noise, as can be seen from the
error curves labelled with VG in Fig. 3. In the length gauge, however, there is a strong dependence on the origin and basis set as can be seen from by comparing the error curves in the AUG-cc-pVDZ and ANO-RCC-VDZP basis sets labelled with LG. In the ANO-RCC-VDZP error curve in the length 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 produce reliable results while AUG-cc-pVDZ basis set cannot.

IV. CONCLUSION

We have here discussed the consequences of not having the exact eigenfunctions and eigenvalues for $\hat{H}_0$ in perturbation theory. The usual approximations such as projecting the wave function on to a finite basis set and restricting the particle interaction usually used for finding the eigenfunctions and eigenvalues for $\hat{H}_0$ is in fact a way of constructing an approximate or effective zeroth order Hamiltonian $\hat{H}'_0$. It it 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 $\hat{H}'_0$ is 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 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 [20], it is therefore trivial to show that this will hold for any approximative $\hat{H}_0$ which also have a spectrum. The origin independence of the intensities in the velocity gauge therefore always hold irrespectively of the choice of basis set and level of correlation as also demonstrated numerically. In the length gauge the origin independence is, however, not guaranteed and only rely on how well $\hat{H}_0$ reproduce the commutation relations of $\hat{H}_0$ since the exact eigenfunctions and eigenvalues of $\hat{H}_0$ is always known.

The calculation of the intensities presented here can be performed significantly more elegant by calculating the exact expression, from Appendix A as shown by List et al. [31, 32]. Here the multipole expansion is completely avoided and origin independence is also a given in the velocity gauge, as also discussed in Appendix A and [31].
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Appendix A: The exact expressions

Showing the origin independence for the intensities for the exact expression is well known and significantly easier to show than the origin independence for the intensities after the multipole expansion [26]. We will here repeat the derivation for the exact expression for the sake of completeness and to show that this is connected to the discussion in Sections 4.1A and 4.1B. The exact expression in the velocity gauge

$$|T_{0n}(O + a)|^2 = \langle 0| \exp(ik \cdot (r - a))(E \cdot \hat{p})|n\rangle \langle n| \exp(-ik \cdot (r - a))(E \cdot \hat{p})|0\rangle$$

will show exact origin independence provided that the $\hat{H}_0$ under projects snic2014-5-36, snic2015-4-71, snic2015-1-465 and snic2015-1-427.

Using Eq. 13 to transform from the velocity to the length gauge

$$|T_{0n}(O + a)|^2 \approx -\frac{m^2}{\hbar^2} \langle 0| \exp(ik \cdot (r - a))(E \cdot ((r - a)\hat{H}_0 - \hat{H}_0'(r - a)))|n\rangle \times \langle n| \exp(-ik \cdot (r - a))(E \cdot ((r - a)\hat{H}_0 - \hat{H}_0'(r - a)))|0\rangle$$

$$\approx -\frac{m^2}{\hbar^2} \langle 0| \exp(i k \cdot r)(E \cdot (r\hat{H}_0' - \hat{H}_0' r))|n\rangle \times \langle n| \exp(-i k \cdot r)(E \cdot (a\hat{H}_0' - \hat{H}_0' a))|0 \rangle + (\langle n| \exp(-i k \cdot r)(E \cdot (a\hat{H}_0' - \hat{H}_0' a))|0 \rangle \times \langle 0| \exp(i k \cdot r)(E \cdot (r\hat{H}_0' - \hat{H}_0' r))|n\rangle) \times \langle n| \exp(-i k \cdot r)(E \cdot (a\hat{H}_0' - \hat{H}_0' a))|0 \rangle)$$

$$\approx |T_{0n}(O)|^2$$

(A1)

(A2)

gives a second order polynomial in $a$ where the zeroth order gives non-zero contribution and all higher orders are zero since $\hat{H}_0'$ commutes with $a$. If the commutation relations for $\hat{H}_0$ and $\hat{H}_0'$ are the same then the origin independence in the length gauge will hold for the exact expression.

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