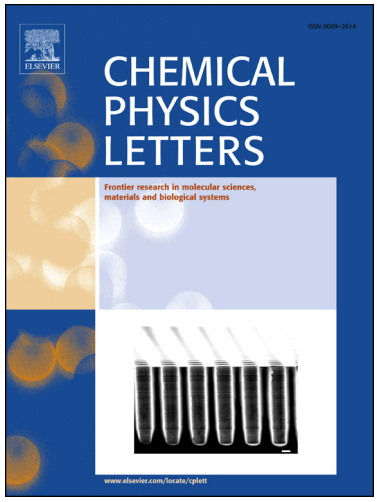

Gauge origin independence in finite basis sets and perturbation theory

Lasse Kragh Sørensen, Roland Lindh, Marcus Lundberg

PII: S0009-2614(17)30434-7
DOI: http://dx.doi.org/10.1016/j.cplett.2017.05.003
Reference: CPLETT 34792

To appear in: *Chemical Physics Letters*

Accepted Date: 2 May 2017

Please cite this article as: L.K. Sørensen, R. Lindh, M. Lundberg, Gauge origin independence in finite basis sets and perturbation theory, *Chemical Physics Letters* (2017), doi: http://dx.doi.org/10.1016/j.cplett.2017.05.003

Gauge origin independence in finite basis sets and perturbation theory

Lasse Kragh Sørensen[a,*], Roland Lindh[a,b], Marcus Lundberg[a]

[a] *Department of Chemistry - Ångström Laboratory, Uppsala University, S-75105 Uppsala, Sweden*
[b] *Uppsala Center of Computational Chemistry - UC$_3$, Uppsala University, S-75105 Uppsala, Sweden*

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-

*Corresponding author
Email address: lasse.kraghsorensen@kemi.uu.se (Lasse Kragh Sørensen)