Light-matter interaction in a relativistic perspective
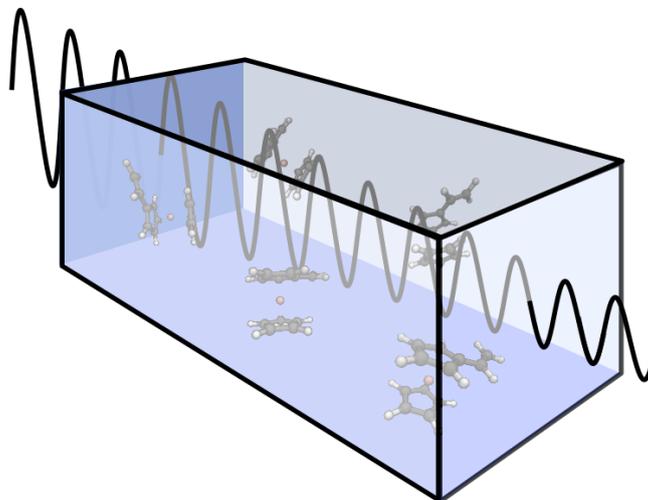
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The importance of relativistic effects in chemistry is illustrated by the fact that without relativity gold would have the same color as silver [1–3], mercury would not be liquid at room temperature [4,5] and your car would not start [6]. The present work highlights another aspect of relativity, namely its essential role in light-matter interaction.

More specifically, we consider relativistic simulations of X-ray absorption spectroscopy. The general expression for the absorption cross sections is

$$\sigma\left(\omega\right) = \frac{\pi\omega}{\varepsilon_0 \hbar c} \left| \langle f | \hat{T}(\omega_{fi}) | i \rangle \right|^2 f\left(\omega, \omega_{fi}, \gamma_{fi}\right),$$

where $\hat{T}(\omega)$ represents light-matter interaction and $f\left(\omega, \omega_{fi}, \gamma_{fi}\right)$ a lineshape function. In the UV/Vis domain the electric dipole approximation is generally employed. In the X-ray domain, its validity is less obvious, since the wave length of the radiation is on the order of molecular dimensions. The usual extension of theory is to include terms beyond zeroth order in the wave vector in the effective interaction operator $\hat{T}\left(\omega\right)$. However, this leads to origin-dependence of absorption cross-sections. In a seminal paper Bernadotte *et al.* showed that this problem is avoided by rather expanding the absorption cross-section $\sigma\left(\omega\right)$ in orders of the wave vector [7]. We have investigated an alternative approach which simply employs the full light-matter interaction [8]. In both approaches rotational averaging has to be considered for isotropic media [9]. In this contribution we consider the extension of these approaches to the relativistic domain.

References

[1] N. Egede Christensen and B. O. Seraphin. Relativistic Band Calculation and the Optical Properties of Gold. *Phys. Rev. B*, 4:3321–3344, Nov 1971.

[2] P. Romaniello and P. L. de Boeij. The role of relativity in the optical response of gold within the time-dependent current-density-functional theory. *The Journal of Chemical Physics*, 122(16):164303, 2005.

[3] Kathrin Glantschnig and Claudia Ambrosch-Draxl. Relativistic effects on the linear optical properties of Au, Pt, Pb and W. *New Journal of Physics*, 12(10):103048, 2010.

[4] Florent Calvo, Elke Pahl, Michael Wormit, and Peter Schwerdtfeger. Evidence for Low-Temperature Melting of Mercury owing to Relativity. *Angewandte Chemie International Edition*, 52(29):7583–7585, 2013.

[5] Krista G. Steenbergen, Elke Pahl, and Peter Schwerdtfeger. Accurate, Large-Scale Density Functional Melting of Hg: Relativistic Effects Decrease Melting Temperature by 160 K. *The Journal of Physical Chemistry Letters*, 8(7):1407–1412, 2017.

[6] Rajeev Ahuja, Andreas Blomqvist, Peter Larsson, Pekka Pyykkö, and Patryk Zaleski-Ejgierd. Relativity and the Lead-Acid Battery. *Phys. Rev. Lett.*, 106:018301, Jan 2011.

[7] S. Bernadotte, A. J. Atkins, and C. R. Jacob. Origin-Independent Calculation of Quadrupole Intensities in X-Ray Spectroscopy. *J. Chem. Phys.*, 137:204106, 2012.

[8] Nanna Holmgaard List, Joanna Kauczor, Trond Saue, Hans Jørgen Aagaard Jensen, and Patrick Norman. Beyond the electric-dipole approximation: A formulation and implementation of molecular response theory for the description of absorption of electromagnetic field radiation. *The Journal of Chemical Physics*, 142(24):244111, 2015.

[9] Nanna Holmgaard List, Trond Saue, and Patrick Norman. Rotationally averaged linear absorption spectra beyond the electric-dipole approximation. *Molecular Physics*, 115(1-2):63–74, 2017.