




 Cite this: *Phys. Chem. Chem. Phys.*,
2025, 27, 6832

 Received 14th January 2025,
Accepted 28th February 2025

DOI: 10.1039/d5cp00178a

rsc.li/pccp

Magnetically induced current density from numerical curls of nucleus independent chemical shifts

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Instead of computing magnetically induced current densities (MICD) *via* the wave function and their quantum mechanical definition, one can also use the differential form of the Ampère–Maxwell law to obtain them from curls *via* spatial derivatives of the induced magnetic field. In magnetic molecular response calculations, the latter can be done by taking the numerical derivative of the so-called “nucleus-independent chemical shifts” (NICS), which are implemented in many standard quantum chemical programs. The resulting numerical MICD data is in contrast to any other first-principles based numerically obtained MICDs computed *via* the wave function route, virtually divergence-free.

At the conclusion of the fourth and final paper in Schrödinger’s seminal series “Quantisierung als Eigenwertproblem”,¹ he introduced a vector quantity that is bilinear in the wave function and its complex conjugate similarly to the density function. He interpreted this quantity as the current density (*Stromdichte*) associated with the probability density (*Gewichtsfunktion*) in configuration space. Schrödinger further concluded that this current density vanishes for nondegenerate energy eigenstates, leading to his strikingly simple explanation of the radiationlessness of atomic ground states.

The current density (CD), denoted by \mathbf{J} , has been of central importance to quantum theory from its earliest days to the present. For the one-particle case, it is defined as

$$\mathbf{J} := \Re\{\psi^* \pi \psi\} \quad (1)$$

where ψ is the quantum mechanical wave function describing the state of the particle, and π is the canonical momentum operator (which itself corresponds to the conjugate of a spatial degree of freedom of the Lagrangian). Today, the CD plays a critical role in theoretical chemistry, as it encodes the complete

information on the molecular magnetic response.^{2–4} All physical magnetic properties, such as magnetic susceptibilities and shielding constants, can be derived directly from the CD.

In quantum chemistry, the computation of \mathbf{J} has traditionally relied on Schrödinger’s original defining equation, using the wave function as the starting point within a first-principles framework based purely on quantum mechanics.[†] Virtually all quantum chemical codes and programs to date (except GIMIC⁷ which is based on the Biot–Savart equation) employ this approach.³ We propose an alternative strategy inspired by Hirschfelder’s notion that his so-called “subobservables”⁸ can be treated analogously to classical quantities.² This perspective, in conjunction with the electrodynamic field equations, provides a fresh framework for deriving \mathbf{J} , potentially opening up new computational and conceptual pathways.

Electrons in a molecule respond to an external magnetic field \mathbf{B}^{ext} by inducing a secondary magnetic field \mathbf{B}^{ind} such that in every point in space \mathbf{r} , a total magnetic field $\mathbf{B}^{\text{tot}} = \mathbf{B}^{\text{ext}} + \mathbf{B}^{\text{ind}}$ results. These fields are related *via* the so-called “nuclear magnetic shielding tensor” $\sigma(\mathbf{r})$, describing the magnetic response of the molecule,

$$\mathbf{B}^{\text{tot}}(\mathbf{r}) = (\mathbf{1} - \sigma(\mathbf{r})) \cdot \mathbf{B}^{\text{ext}}(\mathbf{r}) \quad (2)$$

$$= \mathbf{B}^{\text{ext}}(\mathbf{r}) - \underbrace{\sigma(\mathbf{r}) \cdot \mathbf{B}^{\text{ext}}(\mathbf{r})}_{=\mathbf{B}^{\text{ind}}(\mathbf{r})} \quad (3)$$

The nuclear magnetic shielding tensor can be directly related to the “nucleus-independent chemical shift” tensor or NICS^{9,10} *via*:

$$\sigma(\mathbf{r}) = - \begin{pmatrix} \text{NICS}_{xx}(\mathbf{r}) & \text{NICS}_{xy}(\mathbf{r}) & \text{NICS}_{xz}(\mathbf{r}) \\ \text{NICS}_{yx}(\mathbf{r}) & \text{NICS}_{yy}(\mathbf{r}) & \text{NICS}_{yz}(\mathbf{r}) \\ \text{NICS}_{zx}(\mathbf{r}) & \text{NICS}_{zy}(\mathbf{r}) & \text{NICS}_{zz}(\mathbf{r}) \end{pmatrix}, \quad (4)$$

where the first index refers to the response of the molecule in direction α when the magnetic field points in the β direction (the second index). In tensor notation, this equals to

$$\sigma_{\alpha\beta} = -\text{NICS}_{\alpha\beta} \quad (5)$$

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where α and β (and below also γ and δ) denote the tensor component indices for x, y, z . As already has been outlined in ref. 11 the rank-2 current density susceptibility tensor $\mathcal{J}_{\alpha\beta}$ (CDT) can be expressed *via* the magnetostatic Ampère–Maxwell law (in its differential form) and the NICS tensor (see eqn (4)) as

$$\mu_0 \mathcal{J}_{\alpha\beta}(\mathbf{r}) = \varepsilon_{x\gamma\delta} \nabla_\gamma \text{NICS}_{\delta\beta}(\mathbf{r}) \quad (6)$$

where ε refers to the Levi-Civita tensor, μ_0 is the vacuum susceptibility and summation over repeated Greek indices is implied. This expression is equivalent to eqn (6) from ref. 11 except that we have replaced σ by $-\text{NICS}$ (eqn (5)) according to its definition.⁹ The computation of the NICS tensor and closely related derived quantities is implemented in many common quantum chemical codes, including the efficient mpshift¹² module of Turbomole.^{13–15} It is independent of a prior determination of the current density (susceptibility).

Eqn (6) thus offers a new route for the computation of current densities. Analytical positional derivatives of NICS are not implemented in any quantum chemical codes to the best of our knowledge. However, we found that numerical derivation is a feasible alternative to obtain MICDs. One can formalize a numerical approximation ${}^d\nabla_\gamma$ to the differentiation operator ∇_γ by defining an operator for the finite difference quotient between a forward difference of a vector field component $v_\alpha(\mathbf{r})$ at position \mathbf{r} and a finite numerical increment $d > 0$

$${}^d\nabla_\gamma v_\alpha(\mathbf{r}) = \frac{v_\alpha(\mathbf{r} + d\mathbf{e}_\gamma) - v_\alpha(\mathbf{r})}{d}, \quad (7)$$

with \mathbf{e}_γ being the unit vector along the γ component. Note that this operator depends explicitly on the increment size d and that (under suitable conditions on the operand) $\lim_{d \rightarrow 0} {}^d\nabla_\gamma = \nabla_\gamma$ holds. Thus, the main result of this work can be expressed as

$$\mathcal{J}_{\alpha\beta} \approx \tilde{\mathcal{J}}_{\alpha\beta} = \mu_0^{-1} \varepsilon_{x\gamma\delta} {}^d\nabla_\gamma \text{NICS}_{\delta\beta}, \quad (8)$$

where $\tilde{\mathcal{J}}$ is a numerical approximation to the CDT. For the limit case of d approximating 0, eqn (6) is exactly recovered from eqn (8).

An intriguing property of the current density fields $\tilde{\mathcal{J}}$ derived from the contraction of the approximate CDT with the external magnetic field,

$$\tilde{\mathcal{J}}_\alpha = \tilde{\mathcal{J}}_{\alpha\beta} B_\beta^{\text{ext}}, \quad (9)$$

or

$$\tilde{\mathbf{J}} = \tilde{\mathcal{J}} \cdot \mathbf{B}^{\text{ext}}, \quad (10)$$

lies in its ability to maintain the analytical and defining property of \mathbf{J} —namely that it is divergence-free

$$\nabla \cdot \tilde{\mathbf{J}} = 0 \quad (11)$$

for any stationary eigenstate of the system, provided that the numerical representation of the NICS field is sufficiently smooth. This behaviour contrasts with other numerical approximations ($\tilde{\mathbf{J}}$) to \mathbf{J} obtained from standard quantum chemical software,³ which are essentially based on expression eqn (1). Substantial deviations from zero-divergence arise in calculations based on

incomplete basis sets and for example perturbative expansions (*vide infra*). This is particularly noteworthy because non-zero divergences can pose significant challenges for topological analyses, highlighting the importance of careful numerical treatment. This situation is opposed to by quantum mechanical systems which can be solved analytically or purely theoretical considerations which are independent of numerical data.

At this point, it becomes apparent that $\tilde{\mathbf{J}}$ is not equal to the CD obtained from numerical approximations $\tilde{\tilde{\mathbf{J}}}$ of the magnetically perturbed wave function and the original definition (eqn (1)) by Schrödinger. Monaco, Summa, Zanasi and RB have elaborated on this subject in ref. 11. In short, unlike $\tilde{\mathbf{J}}$, approximations of type $\tilde{\tilde{\mathbf{J}}}$ contain a spurious contamination which can be described as the gradient of the Poisson potential of the spurious non-zero divergence,

$$\varphi_{\text{spurious}} = -\frac{1}{4\pi} \int \frac{\nabla' \cdot \tilde{\tilde{\mathbf{J}}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \quad (12)$$

Subtraction of the term then yields $\tilde{\mathbf{J}}$,¹¹

$$\tilde{\mathbf{J}} = \tilde{\tilde{\mathbf{J}}} - \nabla \varphi_{\text{spurious}} \quad (13)$$

where now $\nabla \cdot \tilde{\mathbf{J}} = 0$. A handful of exemplary calculations of $\tilde{\mathbf{J}}$ are reported and discussed in detail in ref. 11, so we will show only one example calculation on the benzene molecule performed using Turbomole 7.8^{13–15} for the magnetic response and NICS calculations as follows.

The calculations were performed at the DFT level with the BP86^{16,17} functional and the def2-TZVP basis set. The ‘numerical curl’ of the nucleus-independent chemical shieldings was computed on a grid in the molecular plane according to eqn (8) and generated using a Python script.† A plot of the obtained $\tilde{\mathbf{J}}$ vectors is shown in Fig. 1, along with a plot (Fig. 2) of $\tilde{\tilde{\mathbf{J}}}$ obtained with GIMIC,^{7,18} which we denote as $\mathbf{J}^{\text{GIMIC}}$ in the following. The differences of the currents from the two methods ($\tilde{\mathbf{J}} - \mathbf{J}^{\text{GIMIC}}$) are shown in Fig. 3), and the divergence of the current density obtained from GIMIC at the same level of theory ($\nabla \cdot \mathbf{J}$) is shown in Fig. 4.

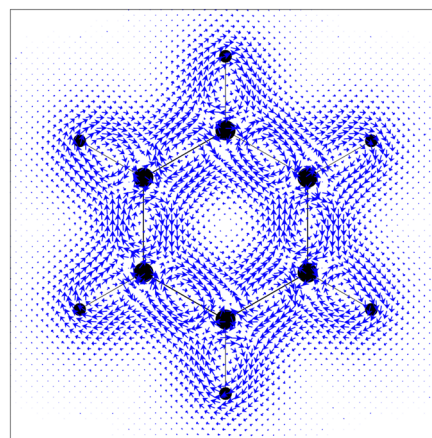


Fig. 1 $\tilde{\mathbf{J}}$ computed *via* eqn (8) in the molecular plane of a benzene molecule on a square grid in steps of 0.6 bohr.



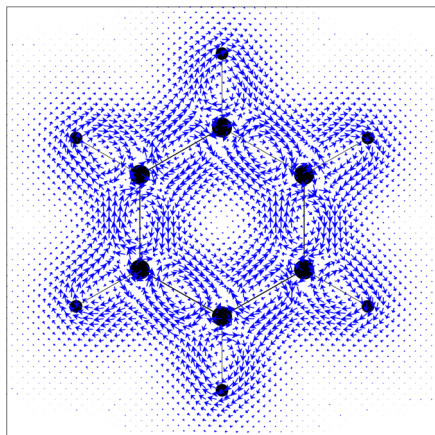


Fig. 2 $\mathbf{J}^{\text{GIMIC}}$ computed with GIMIC in the molecular plane of a benzene molecule on a square grid in steps of 0.6 bohr.

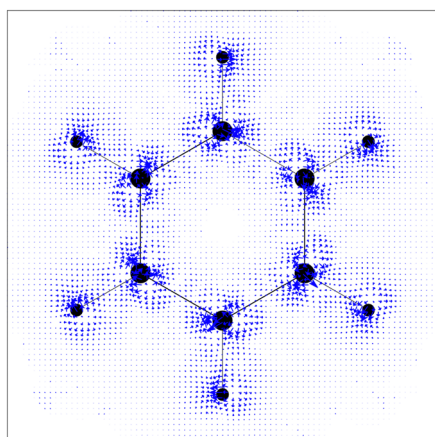


Fig. 3 $\mathbf{J} - \mathbf{J}^{\text{GIMIC}}$ in the molecular plane of a benzene molecule on a square grid in steps of 0.3 bohr and scaled by a factor of 10 w.r.t Fig. 1 and 2.

Prima vista the differences between \mathbf{J} (Fig. 1) and $\mathbf{J}^{\text{GIMIC}}$ (Fig. 2) seem only minor; however, upon subtraction (and upscaling), the differences become more apparent (Fig. 3). As expected, larger deviations appear close to the nuclei. The reason for that is the strong correlation of the differences (explicitly given by eqn (12) and (13)) with the divergence of $\mathbf{J}^{\text{GIMIC}}$. These divergences (*i.e.*, breaking of charge conservation) accumulate close to the nuclei where basis set incompleteness is more pronounced,⁷ which is confirmed by the distribution of $\nabla \cdot \mathbf{J}^{\text{GIMIC}}$ shown in Fig. 4.

In summary, we have devised a new scheme to obtain numerical approximations to the quantum mechanical current density that, unlike previously described methods, does not directly arise from the (perturbed) wave functions but rather from the chemical shift tensor and its spatial derivatives. This approximate CD is virtually divergence-free and can be very simply implemented in any program that can compute chemical shieldings, even interfacing output-data processing scripts. Ongoing work by our groups and collaborators is developing a numerically both efficient and reliable implementation of the

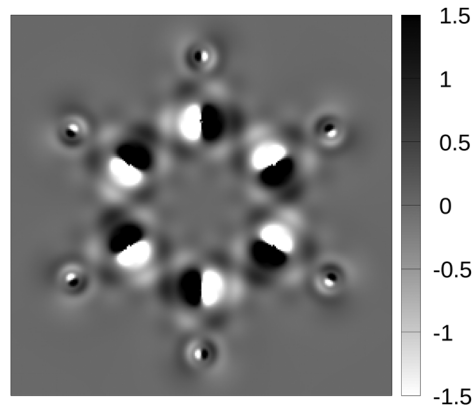


Fig. 4 Divergence of $\mathbf{J}^{\text{GIMIC}}$ ($\nabla \cdot \mathbf{J}^{\text{GIMIC}}$) in the molecular plane of a benzene molecule on a square grid in steps of 0.05 bohr.

scheme proposed here. One key subject thereof will be the choice of the step size of d for the numerical differentiation. We are also currently investigating an approach to decompose \mathbf{J} into components for simplified analyses based on the proposed method.

Author contributions

RB conceived the idea, all other contributions are equally shared among the authors.

Data availability

Data for this article, including a “README” file describing the files and their contents, are available on Zenodo at <https://zenodo.org/records/14902059>.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

RB gratefully acknowledges many insightful discussions with Prof. Dr G. Monaco and Prof. Dr R. Zanasi from the University of Salerno.

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† In contrast, there also exist semi-empirical approaches that rely on parameterization or fitting procedures of simplified models.^{5,6}
‡ The scripts and the data are available at <https://zenodo.org/records/14902059>.

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