Relative energies without electronic perturbations via Alchemical Integral Transform

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We show that the energy of a perturbed system can be fully recovered from the unperturbed system’s electron density. We derive an alchemical integral transform by parametrizing space in terms of transmutations, the chain rule and integration by parts. Within the radius of convergence, the zeroth order yields the energy expansion at all orders, restricting the textbook statement by Wigner that the $p$-th order wave function derivative is necessary to describe the $(2p + 1)$-th energy derivative. Without the need for derivatives of the electron density, this allows to cover entire chemical neighborhoods from just one quantum calculation instead of single systems one-by-one. Numerical evidence presented indicates that predictive accuracy is achieved in the range of mHa for the harmonic oscillator or the Morse potential, and in the range of machine accuracy for hydrogen-like atoms. Considering iso-electronic nuclear charge variations by one proton in all multi-electron atoms from He to Ne, alchemical integral transform based estimates of the relative energy deviate by only few mHa from corresponding Hartree-Fock reference numbers.

I. INTRODUCTION

The energy of a system is central to quantum mechanics, and can be obtained as the solution to the eigenproblem of the Hamiltonian. Solving the electronic Schrödinger equation for real compounds arguably constitutes the most severe bottleneck for our understanding of trends among chemical systems. Unfortunately, the number of conceivably stable materials and molecules is colossal, making brute-force enumeration attempts prohibitive. One possible alternative is to connect the solutions of two chemically distinct systems via continuous interpolation of nuclear charges, aka "alchemy" changes16, as introduced by E. B. Wilson already in 196217. Alchemical Perturbation Density Functional Theory (APDFT)18 couples the Hamiltonians of two iso-electronic systems with a mixing parameter $\lambda$ and generates approximations of relative energies as a perturbative series.19 For sufficiently small changes in chemical position, this series has recently been demonstrated to converge beyond numerical precision20. By virtue of the Hellmann-Feynman theorem (cf. Eq. 1), this perturbative expansion relies exclusively on electron density and derivatives w.r.t. $\lambda$. Perturbations of the electron density at any order are typically calculated explicitly (cf. Eq. 3) via e.g. finite differences4,8 or coupled-perturbed equations9–12, imposing significant computational cost. Recent implementations of automatic differentiation13 in numerical libraries14–17 and even in dedicated quantum chemistry software18–21 hold substantial promise to accelerate APDFT based exploration campaigns of materials compounds space22.

In computational catalysis, alchemy has been used for binding energy predictions with great effect up to first perturbative order.23 A density-derivative-free approach would achieve additional accuracy by naturally including higher orders without an increase in computational cost.

Here, the initial, unperturbed electron density is shown to include sufficient quantum mechanical information to recover the relative energy with respect to any iso-electronic final system – as long as the alchemical ex-
pansion converges. The calculation of density-derivatives therefore becomes unnecessary. This represents a substantial improvement over Wigner’s textbook statement that the \( p \)-th order wave function derivative describes the \((2p + 1)\)-th energy derivative. Below, we provide the derivation and its discussion, followed by numerical results. In particular, we have considered iso-electronic relations and its discussion, followed by numerical results. In particular, we have considered iso-electronic rel-

II. THEORY

The starting point of our formulation is APDF\cite{2020JCP...153l4105P}. Consider any two iso-electronic systems with their electronic Hamiltonians \( \hat{H}_A \) and \( \hat{H}_B \) with corresponding external potentials \( v_A \) and \( v_B \) which are connected via a linear transformation such that \( \hat{H}(\lambda) = \hat{H}_A(1 - \lambda) + \hat{H}_B\lambda \) and \( v(\lambda) = v_A(1 - \lambda) + v_B\lambda \). Given a general electron density \( \rho(\lambda, r) \), which yields the electron density at any \( \lambda \in [0,1] \), the first order derivative according to the Hellmann-Feynman theorem corresponds to

\[
\frac{\partial E(\lambda)}{\partial \lambda} = \langle \Psi_A | \hat{H}_B - \hat{H}_A | \Psi_A \rangle = \int_{\mathbb{R}^3} dr \ \Delta v \ \rho(\lambda, r) \quad (1)
\]

with difference in external potentials \( \Delta v = v_B - v_A \).

We express \( E_B = \langle \Psi_B | \hat{H}_B | \Psi_B \rangle \) by perturbatively expanding \( E(\lambda) = \langle \Psi_A | \hat{H}(\lambda) | \Psi_A \rangle \) at \( \lambda = 0 \). Inserting Eq. 1) into the perturbative expansion

\[
\Delta E := E_B - E_A = \sum_{p=1}^{\infty} \frac{1}{p!} \left. \frac{\partial E(\lambda)}{\partial \lambda} \right|_{\lambda=0} \Delta \lambda^p = \sum_{p=1}^{\infty} \frac{1}{p!} \int_{\mathbb{R}^3} dr \ \Delta v \ \rho^{p-1}(\lambda, r) \quad (2)
\]

with energy difference \( \Delta E = E_B - E_A \). This formula can be rewritten by transferring the \( \lambda \)-dependency of the general \( \rho(\lambda, r) \) to a parametrization of the spatial coordinates \( r(\lambda) \).

As a simplified introduction to the concept and its subsequent generalization, let us first consider the one-dimensional case (in \( r \)) of Eq. 2) for the first non-linear order \( (p = 2) \) with \( r_A := r(\lambda = 0) \). Parametrizing \( r \rightarrow r(\lambda) \) with Jacobian \( J \):

\[
\Delta E^{(2)} = \frac{1}{2} \int_{\mathbb{R}} \! dr(\lambda) J \Delta v(\lambda) \frac{\partial \rho(\lambda, r(\lambda))}{\partial \lambda} \bigg|_{\lambda=0} \quad (4)
\]

Rewriting \( \rho(\lambda, r(\lambda)) = \rho(r^{-1}(\lambda)), \lambda(\lambda)) =: \tilde{\rho}(\lambda(\lambda)) \) and using the chain rule:

\[
\Delta E^{(2)} = \frac{1}{2} \int_{\mathbb{R}} \! dr(\lambda) J \Delta v(\lambda) \frac{\partial \tilde{\rho}(\lambda(\lambda))}{\partial \lambda(\lambda)} \frac{\partial \lambda(\lambda)}{\partial \lambda} \bigg|_{\lambda=0} \quad (5)
\]

When integrating by parts, all limit terms equal zero since the electron density vanishes at infinite distance and \( \partial, J = 0 \). Inserting \( \lambda = 0 \) wherever possible \( (J|_{\lambda=0} = 1) \):

\[
\Delta E^{(2)} = -\frac{1}{2} \int_{\mathbb{R}} \! dr_A \rho_A(r_A) \frac{\partial \Delta v(r_A)}{\partial r_A} \frac{\partial \lambda(\lambda)}{\partial \lambda} \bigg|_{\lambda=0} \quad (6)
\]

\textit{Vide infra} for our general \textit{Ansatz} of \( \partial_A r_A \big|_{\lambda=0} \) for all orders (Eq. 1) and of the full parametrization (Eq. 1).

We now generalize this by applying Faa di Bruno’s formula (repeated chain rule) for composite functions with a vector argument\cite{2011arXiv1109.5712W} to obtain any derivatives of \( \rho \) w.r.t. \( r(\lambda) \) and \( r(\lambda) \) w.r.t. \( \lambda \). Again, all derivatives of \( \rho \) w.r.t. \( r(\lambda) \) equal zero through repeated partial integration, as all spatial derivatives of the electron density vanish at infinite distance (cf. Supplemental Material for the detailed derivation):
Here, we denote the three spatial variables $w_A \in \{x, y, z\}$. The subscript $A$ is needed to discriminate between $w_A$ and the parametrization of the general coordinates $w(\lambda)$, including its derivatives in $\theta_{w,1}$ which emerge from repeated use of the chain rule. Note that $\mathcal{K}$ now includes derivatives of general spatial coordinates $w(\lambda)$ w.r.t. $\lambda$ which is akin to morphing space, or rather repositioning the values of $\rho_A$. Although both initial and final system are described by stationary Hamiltonians, this parametrization in $\lambda$ suggests a mathematical treatment in four dimensions $\lambda, x, y, z$ rather than three, where (possibly non-integer) nuclear charges $Z$ enjoy attention at par with the coordinates, reminiscent of the aforementioned four-dimensional electron density introduced by Wilson. Note that the energy difference $\Delta E$ in Eq. (7) does not depend on a general $\rho(\lambda, r)$ or its derivatives anymore but only on the initial $\rho_A$ and a function $\mathcal{K}(r, v_A, v_B)$. Furthermore, $\Delta E$ is not perturbative in $\rho(\lambda, r)$ anymore, but rather in $\Delta v$ which is known analytically. Even without an explicit expression for $\theta_{w,1}$, this heavily constrains the statement of Wigner’s $(2p+1)$-theorem of perturbation theory: "the first $p$ perturbative eigenfunctions are sufficient to produce the first $2p+1$ eigenenergy derivatives." Now, the zeroth order ($p = 0$) generates all energy derivatives and hence, renders density derivatives obsolete – within the radius of convergence.

Emphasizing its algebraic characteristics and applicability for calculation of energy differences without density derivatives, we henceforth dub this method Alchemical Integral Transform (AIT) since Eq. (7) constitutes an integral transform with non-linear kernel $\mathcal{K}(r_A, v_A(r_A), v_B(r_A))$. Assuming the parametrization $r(\lambda)$ to be analytical on $[0, 1]$ and bijective in an environment of $\lambda = 0$ (cf. Eq. (13)), AIT is rigorous for iso-electronic changes. The AIT in Eq. (7) proves the hypothesis that the unperturbed initial density might suffice for calculating relative energies, as introduced and empirically corroborated in 2009 using non-linear interpolations in $\lambda$. Non-linear $\lambda$-interpolations were also already used within the context of free energy perturbation estimates relying on molecular dynamics based sampling. Relative energies according to AIT are illustrated in Fig. 1 for the alchemical increase in nuclear charge of atoms.

We now propose the following Ansatz for $\theta_{w,1}$ based on dimensional arguments,

$$\theta_{w,1} = \left(1 - \frac{v_B(r_A)}{v_A(r_A)}\right)^i \cdot w_A,$$  

(11)

where $v_A$ and $v_B$ correspond to the known external potentials of any pair of iso-electronic systems. As we gathered all derivatives of the parametrization $r(\lambda)$ at $\lambda = 0$ through Eq. (11) we can construct $r(\lambda)$ via its Maclaurin series:

$$r(\lambda) = \sum_{i=0}^{\infty} \frac{\partial^i r(\lambda)}{\partial \lambda^i} \bigg|_{\lambda=0} \cdot \lambda^i = r_A - \sum_{i=1}^{\infty} \theta_{w,1} \lambda^i,$$  

(12)

$$r(\lambda) = \left(2 - \frac{v_A}{v_B - v_A}\right) r_A$$  

(13)

This parametrization fulfills both bijectivity and invertibility in $\lambda$ on $[0, 1]$ at almost every $r_A$. By explicitly stating $\theta_{w,1}$, Eqs. (7) to (13) provide not just an existence proof for a restriction of Wigner’s $(2p+1)$-theorem, but now serve as a method capable of quantitative predictions. Matching relative energies of analytically solvable models like the hydrogen-like atom, the quantum harmonic oscillator, the Morse potential or the Dirac well
Figure 1. Visualization of the Alchemical Integral Transform (AIT) for radial electron densities and kernel $\mathcal{K}$ corresponding to iso-electronic alchemical changes, exemplified for atoms $H \rightarrow He^+$, $He \rightarrow Li^+$, $O \rightarrow F^+$.

The general convergence behavior of the alchemical Taylor expansion is not rigorously proven except for special case\(^4\), but numerical evidence points towards large convergence radii of the alchemical Taylor expansion even for large changes in external potential\(^7\), also crucially impacted by the quality of the basis set (vide infra). For $v_B$ exceeding $v_A$ in mono-atomic systems beyond this convergence criterion, one can observe the resulting divergence in the Supplemental Material (Fig. 7).

### III. RESULTS

In the following, and without any loss of generality, we restrict ourselves to the case of atoms, $v_B/v_A \rightarrow Z_B/Z_A$, which we show to be correct up to numerical precision in case of the hydrogen-like atom (Fig. 2) and to be applicable to multi-electron atoms (Fig. 3). In the hydrogen-like atom, energy, wave function, and electron density are analytically known. From an initial atom $Z_A$, we transmute to some final $Z_B$ (in atomic units) with principal quantum number $n$:

$$\Delta E_{\text{exact}} = -\frac{Z_B^2 - Z_A^2}{2n^2}$$

Using AIT (cf. Supplemental Material) provides strong evidence that Eqs. (11) to (13) hold for general systems.

From Eqs. (8), (11) and (12), a convergence condition can be read off:

$$\left| 1 - \frac{v_B(r_A)}{v_A(r_A)} \right| < 1 \quad \forall r_A \in \mathbb{R}^3 \quad (14)$$

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AIT and the original perturbative energy expansion match order-wise. This enables the evaluation of energy-perturbations $\partial^p E(\lambda)|_{\lambda=0}$ at selected orders $p$ and gives access to all proportional quantities, e.g. the alchemical potential $\partial_Z E_A$ and the spatial gradient $\partial_{R_A} E_A$ at first order ($p = 1$), or the alchemical hardness $\partial_Z^2 E_A$ (vide infra) and the spatial Hessian $\partial^2_{R_A} E_A$ at second order ($p = 2$)\(^2\).

Analytical higher order energy derivatives have already been presented in the context of Kohn-Sham-DFT\(^9\).

We want to point out that AIT is not limited to Coulombic potentials in three dimensions, but can be shown (cf. Supplemental Material) to be applicable for the Dirac delta well, the quantum harmonic oscillator and the Morse potential, each in one dimension. At the same place, we show that AIT can be generalized to periodic systems in arbitrary dimensions. This provides a strong indication that AIT holds for a wide range of general initial and final potentials, which are not necessarily of the same functional form, but can be of arbitrary finite dimensionality.
AIT simplifies drastically in radially symmetric systems:

\[
\Delta E_{\text{AIT}} = \sum_{p=1}^{\infty} \frac{1}{p} \sum_{T_p} \left( \frac{-1}{\prod_{i=1}^{p-1} k_i !} \right) (-Z_B + Z_A) \left( 1 - \frac{Z_B}{Z_A} \right)^{p-1} 
\times \int_{0}^{\infty} dr_A 4\pi r_A \tilde{\rho}_A(r_A, n, Z_A)
\]  \hspace{1cm} (16)

\[
T_p := \left\{ \mu_r, k_1, \ldots, k_{p-1} \in \mathbb{N}_0 \left| p-1 = \sum_{i=1}^{p-1} i \cdot k_i, \mu_r = \sum_{i=1}^{p-1} k_i \right. \right\}
\]  \hspace{1cm} (17)

The derivation and the spherically averaged electron density \( \tilde{\rho}_A \) are given in the Supplemental Material. In Fig. 2, \( \Delta E_{\text{exact}} \) is compared with \( \Delta E_{\text{AIT}} \) up to and including fifth perturbation order \( p \), fifth state \( n \), and for all transmutations between the first five elements in the periodic table (H, He\(^+\), Li\(^2+\), Be\(^3+\), B\(^4+\)) with \( Z_A < Z_B \). We find the two results to agree with numerical precision (10\(^{-14}\) Ha).

As both energy expressions (Eqs. 15 and 16) match, we find connections between nuclear charges and the radial expectation value of the electron density:

\[
\frac{Z_B + Z_A}{2n^2} = \sum_{p=1}^{\infty} \frac{1}{p} \sum_{T_p} \left( \frac{-1}{\prod_{i=1}^{p-1} k_i !} \right) (-1)^{\mu_r} \mu_r ! \left( 1 - \frac{Z_B}{Z_A} \right)^{p-1} 
\times \int_{0}^{\infty} dr_A 4\pi r_A \tilde{\rho}_A(r_A, n, Z_A)
\]  \hspace{1cm} (18)

and in the limit of \( Z_B \rightarrow Z_A \),

\[
\frac{Z_A}{4\pi n^2} = \int_{0}^{\infty} dr_A r_A \cdot \tilde{\rho}_A(r_A, n, Z_A) =: \langle \tilde{\rho}_A \rangle_{r_A}
\]  \hspace{1cm} (19)

Fig. 2. AIT for the hydrogen-like atom: the analytically known energy \( \Delta E_{\text{exact}} \) scattered against the AIT energy \( \Delta E_{\text{AIT}} \) up to and including fifth perturbation order \( p \) for different quantum numbers \( n \) where initial and final nuclei \( Z_A, Z_B \in \{1, 2, 3, 4, 5\} \) (H, He\(^+\), Li\(^2+\), Be\(^3+\), B\(^4+\)), and \( Z_A < Z_B \). The numbers agree within 10\(^{-14}\) Ha. Radial electron densities of H for different \( n \) are shown in the inset.

This relation holds even for multi-electron atoms.

AIT for systems with more than one electron is inherently more challenging because \( \Delta E_{\text{AIT}} \) depends on \( \rho_A \) and numerical electron densities of a multi-electron system are only known approximately (cf. Fig. 7 in the Supplemental Material). Thus, accuracy suffers from approximations made to the electron correlation problem, as well as from incomplete basis set effects (Pulay-forces\(^\text{[29]}\)), as shown in Refs. [4] and [30]. Approaching the complete
Our comparison of $\Delta E_{\text{AIT}}$ and $\Delta E_{\text{SCF}}$ for different basis sets with the basis functions fixed to the individual initial atom indicates that accuracy benefits the most from using Hartree-Fock with the def2-TZVP basis functions of Xe (details given in the Supplemental Material). To make this selection, we have tested different combinations of basis sets (of the families Pople, Dunning-Douglas-Kroll, Dunning JK-fitting, Ahlrichs, Lehtola, ANO and STO\cite{33}), basis functions, and different levels of theory in terms of treating electron correlation (HF, ROHF, CISD, CCSD, and FCI). We always encounter a mean average error (MAE) of at least 50 mHa when performing benchmarks on the elements H to Ne and $\Delta Z = \pm 1$.

Similar discrepancies in accuracy among basis sets for elements have also been seen before for alchemical derivatives involving noble gases\cite{32}.

For an overarching picture of AIT’s accuracy for multi-electron-atom predictions, we have used the best-performing basis set, def2-TZVP with the basis functions of Xe, to quantify the absolute error $\Delta \Delta E = \Delta E_{\text{SCF}} - \Delta E_{\text{AIT}}$ for iso-electronic interpolations where $1 \leq Z_A, Z_B \leq 10$. Fig. 3 displays prediction errors as a heat map for all atoms $Z_A$ from H up to Ne, with $Z_B = Z_A \pm dZ$ with $dZ \in \{1, 2\}$. The number of electrons $N_e$ of the initial atom $Z_A$ always equals its nuclear charge such that the overall charge $Q_A = 0$. A version with non-integer $Z_A, Z_B$ can be found in the Supplemental Material. The energies of e.g. $N^-$ and $F^+$ can be estimated based only on the unperturbed electron density of oxygen within $\sim 19$ and $\sim 24$ mHa, respectively. Especially close to the nucleus, $\Delta E_{\text{AIT}}$ becomes very sensitive to errors in electron density as $\|K\|$ becomes large (cf. Fig. 1). This sensitivity overtly shows when calculating energy differences between H and another hydrogen-like atom: while the approximate self-consistent field (SCF)-solution diverges for $Z_B > 2$ as the basis set has no sufficiently tight basis functions, the analytical solution holds even for $Z_B = 5$ (Fig. 2). This difference in electron densities can be seen in the inset of Fig. 3 for He$^+$. Clearly, the SCF solution suffers in accuracy when stacking positive charges in the nucleus because the basis sets were not designed to properly account for such deformation, as also recently discussed in Ref. 33. Furthermore, there appears to be a sudden change in the sign of $\Delta \Delta E$ between N and O. This trend is identical for arbitrary perturbation orders $p > 2$, hence we reckon this to be not due to truncation or divergence of the series in Eq. 8 but instead the quality of electron densities from Hartree-Fock methods. Increasing the initial density’s quality will be crucial to access the chemical neighborhood with better accuracy.

In summary, we have introduced AIT, the Alchemical Integral Transform that turns a converging perturbative expansion of relative energies in electron density derivatives into an analytical expansion in external potentials and space derivatives. Our Ansatz naturally leads to accurate energy predictions of atoms with neighboring nuclear charges, as demonstrated for hydrogen-like atoms as well as for all atoms up to Ne. As a consequence, we could show that only the initial unperturbed elec-
tron density is required for AIT, rendering negligible the computational cost for accurate estimates of relative energies of distinct iso-electronic systems. In conclusion, all the relevant quantum mechanical information for any iso-electronic system of the same quantum state is already contained in the initial electron density, restricting Wigner’s \((2p + 1)\)-theorem of perturbation theory. Consequently, this constitutes a strong hint to apply alchemical methods in general, and AIT in specific, to obtain also relative electron densities.

Future work will deal with other systems, as a generalization to molecules and materials appears to have great merit to explore vast regions of materials compound space more efficiently based only on few unperturbed electron densities. Our particular Ansatz, the role of electron correlation treatment, as well as basis sets effects (cf. magnitude and sign of \(\Delta \Delta E\) in Fig. 5) and the overall quality of the electron density, might also be worthy of further attention. Especially the latter seems promising to gain accuracy, as an electron density of higher quality may be computationally expensive, but once obtained, enables access to a multitude of (accurate) relative energies.

SUPPLEMENTARY MATERIAL

See the supplementary material for the derivation of Eqs. 7 and 8, the solutions to the linear Diophantine equations (cf. Eq. 10), the functional form of the electron density of the hydrogen-like atom, the derivation of Eq. 16, an alternative proof of Eq. 19, the application of AIT to toy models (Dirac well, quantum harmonic oscillator, Morse potential, periodic potentials) and details regarding the performance of basis sets in multi-electron atoms.

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CONFLICT OF INTEREST

The authors have no conflicts to disclose.

AUTHOR CONTRIBUTIONS

Simon León Krug: conceptualization (lead), data curation, formal analysis (lead), investigation (lead), methodology (lead), software, visualization (equal), writing - original draft (lead), writing - review & editing (supporting). Guido Falk von Rudorff: conceptualization (supporting), formal analysis (supporting), investigation (supporting), methodology (supporting), supervision (supporting), visualization (equal), writing - original draft (equal). O. Anatole von Lilienfeld: conceptualization (supporting), formal analysis (supporting), investigation (supporting), methodology (supporting), funding acquisition, project administration, resources, supervision (lead), visualization (equal), writing - review & editing (lead).

All authors read and approved the final manuscript.

DATA AND CODE AVAILABILITY

The data that support the findings of this study, namely the data basis of Figs. 5 and 9, is openly available on Zenodo and can be found under https://doi.org/10.5281/zenodo.6779769. The code that produces the findings of this study, in specific the comparisons of the hydrogen-like atom, multi-electron atom, quantum harmonic oscillator and Morse potential, are openly available on GitHub under https://github.com/SimonLeonKrug/pyalchemy.

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Relative energies without electronic perturbations via Alchemical Integral Transform
— Supplemental Material —

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I. DERIVATION OF EQS. 7 AND 8

Starting with Eq. 3 we shift the index $p \rightarrow p + 1$:

$$\Delta E = \sum_{p=0}^{\infty} \frac{1}{p!} \int_{\mathbb{R}^3} dr \Delta \cdot \frac{\partial^{p+1} \rho(\lambda, r)}{\partial \lambda^{p+1}} \bigg|_{\lambda = 0} = \sum_{p=0}^{\infty} \frac{1}{(p + 1)!} \int_{\mathbb{R}^3} dr \Delta \cdot \frac{\partial^{p} \rho(\lambda, r)}{\partial \lambda^{p}} \bigg|_{\lambda = 0}$$

(23)

We want to reshape this expression by transferring the $\lambda$-dependency of the general $\rho(\lambda, r)$ to a parametrization of the coordinates $r \rightarrow r(\lambda)$ where $r(\lambda = 0) =: r_0$. We demand this parametrization to be analytic at $\lambda = 0$ and invertible around $\lambda = 0$, with the inverse denoted as $r^{-1} : \mathbb{R}^3 \rightarrow [0, 1]$. Both criteria are fulfilled by the parametrization given in Eq. [13]. The Jacobian of this transform shall be denoted $J$ with property $J|_{\lambda = 0} = 1$.

$$\Delta E = \sum_{p=0}^{\infty} \frac{1}{(p + 1)!} \int_{\mathbb{R}^3} dr \rho(\lambda) J \Delta v(r(\lambda)) \frac{\partial^{p} \rho(\lambda, r(\lambda))}{\partial \lambda^{p}} \bigg|_{\lambda = 0}$$

(24)

Now we rewrite the electron density after the transformation, $\rho(\lambda, r(\lambda))$, as a suitable new function $\tilde{\rho}$:

$$\rho(\lambda, r(\lambda)) = \tilde{\rho}(r^{-1}(r(\lambda)), r(\lambda)) =: \tilde{\rho}(r(\lambda))$$

(25)

$$\Rightarrow \Delta E = \sum_{p=0}^{\infty} \frac{1}{(p + 1)!} \int_{\mathbb{R}^3} dr \rho(\lambda) J \Delta v(r(\lambda)) \frac{\partial^{p} \tilde{\rho}(r(\lambda))}{\partial \lambda^{p}} \bigg|_{\lambda = 0}$$

(26)

Use Faà di Bruno’s formula for composite functions with a vector argument to re-express $\tilde{\rho}(r(\lambda))$ as a chain of $\tilde{\rho} : \mathbb{R}^3 \rightarrow \mathbb{R}^+$ and $r : [0, 1] \rightarrow \mathbb{R}^3$ (chain rule in 3 dimensions for the $p$-th derivative):

$$= \sum_{p=0}^{\infty} \frac{1}{(p + 1)!} \int_{\mathbb{R}^3} dr \rho(\lambda) J \Delta v(r(\lambda)) \sum_{\alpha=1}^{\infty} \sum_{\beta=1}^{\infty} \cdots \sum_{\gamma=1}^{\infty} \prod_{i=1}^{p} \frac{\partial^{p} \tilde{\rho}(r(\lambda))}{\partial x^{(i)}_1} \frac{\partial^{p} \tilde{\rho}(r(\lambda))}{\partial y^{(i)}_1} \frac{\partial^{p} \tilde{\rho}(r(\lambda))}{\partial z^{(i)}_1} \bigg|_{\lambda = 0}$$

(27)
The sums run over all non-negative integer solutions of the following \( p + 1 \) linear Diophantine equations:

\[
\sum_0^1 k_1 + 2k_2 + \cdots + pk_p = p \tag{28}
\]

\[
\sum_1^p q_1^x + q_1^y + q_1^z = k_1 \tag{29}
\]

\[
\vdots
\]

\[
\sum_p^q q_p^x + q_p^y + q_p^z = k_p \tag{30}
\]

Furthermore, the conditions hold:

\[
\mu_x = q_1^x + \cdots + q_p^x \tag{31}
\]

\[
\mu_y = q_1^y + \cdots + q_p^y \tag{32}
\]

\[
\mu_z = q_1^z + \cdots + q_p^z \tag{33}
\]

\[
k = \mu_x + \mu_y + \mu_z = k_1 + \cdots + k_p \tag{34}
\]

Note that this only holds for the first and higher derivatives. In case of \( p = 0 \), the sum \( \sum_0 \) shall be taken over all \( \mu = \mu_x + \mu_y + \mu_z = 0 \) which nicely reproduces the result of Eq. [3] for \( p = 0 \).

The chain of \( \bar{\rho} \) and \( r \) holds for general three-dimensional arguments – it is not limited to Cartesian coordinates, i.e. \( r = (r, \theta, \phi) \) with \( dr = r^2 \sin(\theta) \, dr \, d\theta \, d\phi \) is equivalent.

Firstly, we can use the distributivity of summations when summing over different indices. Each \( \sum_i \) only acts on its respective \( k_i, q_i^x, q_i^y, q_i^z \), so the sums factorize; product and sums can be swapped:

\[
\Delta E = \sum_{p=0}^{\infty} \frac{1}{p + 1} \int_{\mathbb{R}^3} dr(r(\lambda)) \Delta x(r(\lambda)) \sum_0^p \frac{1}{\prod_{i=1}^p (i!)^{k_i} k_i!} \frac{\partial^k \bar{\rho}(r(\lambda))}{\partial x^\mu(\lambda) \partial y^\mu(\lambda) \partial z^\mu(\lambda)} \times \prod_{i=1}^p \frac{k_i!}{(q_i^x!)(q_i^y!)(q_i^z!)} \left( \frac{\partial x(\lambda)}{\partial \lambda^i} \right)^{q_i^x} \left( \frac{\partial y(\lambda)}{\partial \lambda^i} \right)^{q_i^y} \left( \frac{\partial z(\lambda)}{\partial \lambda^i} \right)^{q_i^z} \bigg|_{\lambda = 0} \tag{35}
\]

Secondly, we apply the multinomial theorem:

\[
\Delta E = \sum_{p=0}^{\infty} \frac{1}{p + 1} \sum_0^p \frac{1}{\prod_{i=1}^p (i!)^{k_i} k_i!} \int_{\mathbb{R}^3} dr(r(\lambda)) \frac{\partial^k \bar{\rho}(r(\lambda))}{\partial x^\mu(\lambda) \partial y^\mu(\lambda) \partial z^\mu(\lambda)} \times \prod_{i=1}^p \left( \frac{\partial x(\lambda)}{\partial \lambda^i} + \frac{\partial y(\lambda)}{\partial \lambda^i} + \frac{\partial z(\lambda)}{\partial \lambda^i} \right)^{k_i} \bigg|_{\lambda = 0} \tag{36}
\]
Thirdly, we perform $\mu_x, \mu_y, \mu_z$-times integration by parts. All limit terms equal zero because $\partial^\mu \rho_A / \partial u_A^{\mu^e} \rightarrow 0$ as $w_A \rightarrow \pm \infty$ for all $\mu^e \in \mathbb{N}_0$ and $w \in \{x, y, z\}$. Every finite system’s electron density vanishes at infinite distance and so do its spatial derivatives. However, this holds only if $\partial^\mu \rho_A / \partial u_A^{\mu^e}$ decays faster than $\partial^\nu \Delta \psi / \partial u_A^{\mu^e}$ grows.

$$\Delta E = \int_{\mathbb{R}^3} dr_A \rho_A (r_A) \mathcal{K} (r_A, v_A, v_B)$$

$$= \sum_{p=0}^{\infty} \frac{1}{p + 1} \sum_{\delta p} \left( \begin{array}{c} (-1)^p \\
\prod_{i=1}^{p} (d_i)^{k_i} \end{array} \right) \int_{\mathbb{R}^3} dr (r) \rho (r)$$

$$\times \frac{\partial^p}{\partial x (\lambda)^{\mu_x} \partial y (\lambda)^{\mu_y} \partial z (\lambda)^{\mu_z}} \left[ J \Delta \psi (r (\lambda)) \prod_{i=1}^{p} \left( \frac{\partial x (\lambda)}{\partial x (\lambda)} + \frac{\partial y (\lambda)}{\partial y (\lambda)} + \frac{\partial z (\lambda)}{\partial z (\lambda)} \right)^{k_i} \right] \bigg|_{\lambda=0}$$

(37)

Within the brackets, only $\Delta \psi (r (\lambda))$ is non-constant w.r.t. $x (\lambda), y (\lambda), z (\lambda)$ because:

$$\frac{\partial}{\partial x} \prod_{i=1}^{p} \left( \frac{\partial x}{\partial x (\lambda)} + \frac{\partial y}{\partial x (\lambda)} + \frac{\partial z}{\partial x (\lambda)} \right)^{k_i} = \prod_{i=1}^{p} \left( \frac{\partial x}{\partial x (\lambda)} \right) \left[ x + y + z \right]^{k_i} \left( \sum_{k_i \neq 0} \left( \sum_{i} k_i \frac{\partial x}{\partial x (\lambda)} \right) \left[ x + y + z \right] \right) = 0$$

(38)

As $\partial [x + y + z] = 1$, already the first derivative w.r.t $\lambda$ vanishes. The same goes for $y$ and $z$. Furthermore, the Jacobian vanishes, too:

$$\frac{\partial}{\partial x} J = \frac{\partial}{\partial x} \text{det} (J) = \frac{\partial}{\partial x} \text{det} \left( \frac{\partial x}{\partial x}, \frac{\partial x}{\partial y}, \frac{\partial x}{\partial z} \right) = 0$$

(39)

Again, this holds for $y$ and $z$ as well.

Set $\lambda = 0$ wherever possible, revert the index shift from the beginning ($p \rightarrow p - 1$) and use $k = \mu_x + \mu_y + \mu_z$:

$$\Delta E = \int_{\mathbb{R}^3} dr_A \rho_A (r_A) \mathcal{K} (r_A, v_A, v_B)$$

(40)

$$\mathcal{K} (r_A, v_A, v_B) = \sum_{p=0}^{\infty} \frac{1}{p + 1} \sum_{\delta p} \left( \begin{array}{c} (-1)^p \\
\prod_{i=1}^{p} (d_i)^{k_i} \end{array} \right) \left[ \prod_{i=1}^{p-1} \left( \sum_{\theta \in \mathbb{N}_0 \setminus \{0\}} \theta (\lambda) \right)^{k_i} \right]$$

(41)

$$\theta_{w,j} := \left. \frac{1}{i!} \frac{\partial u (\lambda)}{\partial x (\lambda)^{i}} \right|_{\lambda=0}$$

(42)

$$S_p := \left\{ \mu_x, \mu_y, \mu_z, k_1, \ldots, k_{p-1} \in \mathbb{N}_0 \mid p - 1 = \sum_{i=1}^{p-1} i \cdot k_i, \mu_x + \mu_y + \mu_z = \sum_{i=1}^{p-1} k_i \right\}$$

(43)

Eqs. 23 and 40 match order-wise.
## II. SOLUTIONS TO THE LINEAR DIOPHANTINE EQUATIONS

Below are a list of the first few $(3 + (p - 1))$-tuples of $S_p$:

$$p \quad | \quad \mu_1, \mu_2, \mu_3, k_1, \ldots, k_{p+1}$$

1. $[0, 0, 0]$  
2. $[1, 0, 0, 1, 0, 0, 0, 0]$  
3. $[0, 0, 0, 0, 0, 0, 0, 0]$  
4. $[0, 0, 0, 0, 0, 0, 0, 0]$  
5. $[0, 0, 0, 0, 0, 0, 0, 0]$  
6. $[0, 0, 0, 0, 0, 0, 0, 0]$  

\[ \cdots \cdots \]

## III. ELECTRON DENSITY OF HYDROGEN-LIKE ATOM

The solutions of the hydrogen-like atom with nuclear charge $Z$ and averaged electron density $\bar{\rho}$, depending only on $r$, $n$, and $Z$, is then given by:

$$\bar{\rho}_A(r, n, Z_A) = \frac{1}{n^2} \sum_{l_m} \langle \Psi_{nlm}^\star (r, \theta, \phi) | \delta(r - r_A) | \Psi_{nlm} (r, \theta, \phi) \rangle$$

\[ \text{(46)} \]

\[ \text{(47)} \]
IV. DERIVATION OF EQ. [16]

A simplification for radially symmetric systems can be derived from Eqs. [7] and [8] instead of $x_A, y_A, z_A$, we choose spherical coordinates $r_A, \theta_A, \phi_A$. Since any mono-atomic system is independent of its angles, $\theta_A, \phi_A$ can be dropped in the application of Faà di Bruno’s formula in Eq. [27] and the angular integration $\int d\Omega$ reduces to a constant of $4\pi$. Additionally, the sum over the set $S_p$ reduces to $T_p$ below, as two of three $\mu$’s are zero:

$$\Delta E_{\text{AT}} = \int_0^{\infty} dr_A r_A^2 \int d\Omega \, \rho_A(r_A, n, Z_A) \sum_{p=1}^{\infty} \frac{1}{p} \sum_{\mu_p} \left[ \frac{\partial^{\mu_p} - Z_B + Z_A}{\partial r_A^{\mu_p}} r_A \right] \cdot \left[ \prod_{i=1}^{p-1} \frac{r_i^k}{k_i!} \right]$$

$$= \int_0^{\infty} dr_A \, 4\pi r_A \bar{\rho}_A(r_A, n, Z_A) \sum_{p=1}^{\infty} \frac{1}{p} \sum_{\mu_p} \left( \frac{(-1)^{\mu_p} \cdot \mu_p!}{\prod_{i=1}^{p-1} k_i!} \right) (-Z_B + Z_A) \left( 1 - \frac{Z_B}{Z_A} \right)$$

$$T_p := \{ \mu, k_1, \ldots, k_{p-1} \in \mathbb{N}_0 \mid p - 1 = \sum_{i=1}^{p-1} i \cdot k_i, \mu_p = \sum_{i=1}^{p-1} k_i \} \quad \text{(50)}$$

The first few $g_p$ are:

$$\frac{p}{g_p} = 1 \frac{1}{2} \frac{1}{3} \frac{4}{5} \frac{6}{7} \ldots$$

V. PROOF OF EQ. [19]

Eq. [19] is visualized in Fig. [4]. However, it can also be proven with the following orthogonality relation of the Laguerre polynomial:

$$\int_0^{\infty} dx \, e^{-x} x^k \ell_n^{(k)}(x) \ell_m^{(k)}(x) = \frac{(n + k)!}{n!} \delta_{mn} \quad \text{(51)}$$

Thus, we can write:

$$\frac{Z_A}{4\pi n^2} = \int_0^{\infty} dr_A \, r_A \bar{\rho}_A(r_A, n, Z_A) \quad \text{(52)}$$

$$= \frac{1}{n^2} \sum_{l=0}^{n-1} \frac{2l + 1}{4\pi} \left( \frac{2Z_A}{n} \right)^{(n - l - 1)!} \int_0^{\infty} \frac{dr_A}{n} \left( \frac{2Z_A r_A}{n} \right)^{(2l+1)} \left( \frac{L_{n-l-1}^{(2l+1)}(2Z_A r_A)}{n} \right)^2 \exp \left( -\frac{2Z_A r_A}{n} \right)$$

Substitute $v = 2Z_A r_A/n$:

$$\int_0^{\infty} dv \, e^{-v} v^{2l+1} \left( L_{n-l-1}^{(2l+1)}(v) \right)^2 \quad \text{(54)}$$

$$= \frac{Z_A}{4\pi n^2} \sum_{l=0}^{n-1} (2l + 1) = \frac{Z_A}{4\pi n^2} \sum_{l=0}^{n-1} (2l + 1) = \frac{Z_A}{4\pi n^2}$$
VI. THE DIRAC DELTA POTENTIAL

Consider a particle in the one-dimensional potential of a Dirac delta function

\[ v(x) = -b \cdot \delta(x) \quad b > 0 \quad , \]

with energy eigenvalue and wave functions

\[ E = -\frac{b^2}{2} \quad , \]

\[ \Psi(x) = \sqrt{b} \cdot \exp(-b|x|) \quad . \]

Using AIT to obtain the energy difference between two such systems A and B with well depths \( b_A \) and \( b_B \):

\[ \Delta E_{BA} = \int_{-\infty}^{\infty} dx_A \rho_A(x_A) K(x_A, v_A, v_B) \]

\[ = \int_{-\infty}^{\infty} dx_A b_A \cdot \exp(-2b_A|x_A|) \sum_{p=1}^{\infty} \left( 1 - \frac{b_B}{b_A} \right)^p \frac{p-1}{p} \sum_{T_p} (b_A - b_B) \frac{\partial^{p-1} \delta(x_A)}{\partial x_A^{p-1}} \cdot \left[ \prod_{i=1}^{r} \frac{x_A^{k_i}}{k_i!} \right] \]

\[ = b_A^2 \sum_{p=1}^{\infty} \left( 1 - \frac{b_B}{b_A} \right)^p \frac{p-1}{p} \sum_{T_p} \left[ \prod_{i=1}^{r} \frac{1}{k_i!} \right] \int_{-\infty}^{\infty} dx_A \exp(-2b_A|x_A|) \frac{x_A^{p-1}}{k_i!} \frac{\partial^{p-1} \delta(x_A)}{\partial x_A^{p-1}} \]

with \( T_p \) same as in Eq. 50.
The integral can be evaluated by applying the distributional derivative of the Dirac delta function:

\[
\int_{-\infty}^{+\infty} \frac{1}{\pi} \frac{\omega_B}{\xi} \sum_{\mu=1}^{\infty} \frac{1}{\mu + \frac{1}{2}} \mu! (-1)^{\mu-1} \mu_p \left( 1 - \frac{\xi}{\mu} \right)^{\mu-1} \rho \left( x, v_B + \Lambda_{\text{reg}}, v_A + \Lambda_{\text{reg}} \right) \, dx_A \]  

(61)

… with \( g_p \) same as in Eq. [49]. Similar to the hydrogen-like atom, one can numerically show:

\[
\sum_{\mu=1}^{\infty} g_p \xi^{\mu-1} = 1 - \frac{\xi}{2} \quad \xi \in \mathbb{R} 
\]

(63)

Finally, we obtain the energy difference from AIT:

\[
\Delta E_{BA} = -\frac{b_B^2 - b_A^2}{2} 
\]

(64)

VII. THE QUANTUM HARMONIC OSCILLATOR

Consider the potential of the one-dimensional harmonic oscillator

\[ v(x) = \frac{\omega^2}{2} x^2 \quad \omega > 0 \quad , \]

(65)

with energy eigenvalue and wave functions

\[
E_n = \omega \left( n + \frac{1}{2} \right) 
\]

(66)

\[
\Psi_n(x) = \frac{1}{\sqrt{2^n n!}} \left( \frac{\omega}{\pi} \right)^{1/4} \exp \left( -\frac{\omega x^2}{2} \right) H_n \left( \sqrt{\omega} x \right) \quad . 
\]

(67)

where \( H_n \) are the physicist’s Hermite polynomials\(^{34}\).

Using AIT to obtain the energy difference between two such systems A and B with frequencies \( \omega_A \) and \( \omega_B \) proves to be difficult analytically, as well as numerically. However, the numerical difficulties come from the convergence behavior of the series in \( \mathcal{K}(x, v_B, v_A) \) and can be evaded by adding a regulatory energy constant \( \Lambda_{\text{reg}} \gg \Delta E_{BA} \) to initial and final potential. The energy difference between the systems \( \Delta E_{BA} \) and the wave function are unaffected by this but the convergence behavior of the AIT kernel changes towards more favorable regimes.

With this, Eqs. [68] and [69] equal one another with small numerical error as seen in Fig. [6a]:

\[
\Delta E_{BA} = (\omega_B - \omega_A)(n + \frac{1}{2}) 
\]

(68)

\[
\Delta E_{BA} = \int_{-\infty}^{+\infty} \rho_A(x_A) \mathcal{K} \left( x_A, v_A + \Lambda_{\text{reg}}, v_B + \Lambda_{\text{reg}} \right) \, dx_A 
\]

(69)
VIII. THE MORSE POTENTIAL

Consider the one-dimensional Morse potential centered around $x_0$ with well depth $D$ and range parameter $a$.

$$v(x) = D \cdot (\exp(-2a \cdot (x - x_0)) - 2 \exp(-a \cdot (x - x_0))) \quad D, a > 0 \quad ,$$

with energy eigenvalue and wave functions

$$E_n = \sqrt{2D} a \cdot \left(n + \frac{1}{2}\right) \cdot \left(1 - \frac{a}{2 \sqrt{2D}} \left(n + \frac{1}{2}\right)\right) - D$$

$$\Psi_n(x) = N(z, n) \sqrt{a} e^{-\xi} e^{-\xi/2} L_n^{(2z-2n-1)}(\xi)$$

$$z = \frac{2D}{a}$$

$$\xi = 2z \cdot e^{-a(x-x_0)}$$

$$N(z, n) = \sqrt{\frac{(2z - 2n - 1) \Gamma(n + 1)}{\Gamma(2z - n)}} \quad ,$$

where $L$ are the generalized Laguerre polynomials.

Again, adding a regulatory constant $\Lambda_{\text{reg}}$ to initial and final potential in the AIT kernel enables us to obtain the energy difference $\Delta E_{BA}$ between two systems $A$ and $B$ with small numerical error as seen in Figs. 5 and 6b.
Figure 5. AIT for the three parameters depth $D$, width $a$ and minimum position $x_0$ of the Morse potential: the error $\Delta \Delta E = |\Delta E_{\text{exact}} - \Delta E_{\text{AIT}}|$ between the analytically known energy $\Delta E_{\text{exact}}$ and the AIT energy $\Delta E_{\text{AIT}}$ up to and including fifth perturbation order $p$ for quantum number $n = 0$. The initial system’s parameter are $D_A = 15$, $a_A = 1$, $x_{0A} = 0$ in atomic units.
Figure 6. AIT for two textbook examples of potentials: the analytically known energy $\Delta E_{\text{exact}}$ scattered against the AIT energy $\Delta E_{\text{AIT}}$ up to and including fifth perturbation order $p$, below the error $\Delta \Delta E = |\Delta E_{\text{exact}} - \Delta E_{\text{AIT}}|$ for different quantum numbers $n$. In 6a the quantum harmonic oscillator with $\omega_A, \omega_B \in \{11.0, 11.2, \ldots, 12.0\}$ and $\omega_A < \omega_B$. In 6b the Morse potential centered at $x_0 = 0$ with $a_A = a_B = 1$, $D_A = 22$, $D_B = D_A - dZ$ and $dZ \in \{0.1, 0.2, \ldots, 1.0\}$. 
IX. PERIODIC POTENTIALS IN THE ALCHEMICAL INTEGRAL TRANSFORM

Consider the AIT in \( n \) dimensions with periodic initial and final potentials \( v_A, v_B : \mathbb{R}^n \rightarrow \mathbb{R} \) of \( N_1 N_2 \ldots N_n \) many cells and cell vector \( R \) with length \( L_i = N_i R_i \), such that both can be written as \( n \) sums of a single potential \( v_{\text{cell}} \):

\[
v_{A,B}(r) = \sum_{j_1=0}^{N_1-1} \cdots \sum_{j_n=0}^{N_n-1} v_{\text{cell}}(r_1 + j_1 \cdot R_1, \ldots, r_n + j_n \cdot R_n)
\]  

(76)

As \( L_1, \ldots, L_n \rightarrow \infty \), any central cell experiences only an effective potential \( v_{\text{eff}}^{A,B}(r) \). As all \( N_1 N_2 \ldots N_n \) cells can be treated identically in the limit, one needs to evaluate the integral over \( \mathbb{R}^n \) only for one central cell \( \Omega' = [0, R_1) \times \cdots \times [0, R_n) \), then multiply by the number of cells:

\[
\Delta E_{BA} = \int_{\mathbb{R}^n} dr_A \rho_A (r_A) \mathcal{K} (r_A, v_A, v_B)
\]

\(\Leftrightarrow\)

\[
[N_1 N_2 \ldots N_n] \Delta E_{\text{cell}}^{BA} = [N_1 N_2 \ldots N_n] \int_{\Omega'} dr_A \rho_A (r_A) \mathcal{K} (r_A, v_{\text{eff}}^{A}, v_{\text{eff}}^{B})
\]

(77)

(78)

Dropping the factors of \( N_1 N_2 \ldots N_n \) on both sides gives access to the energy difference per cell \( E_{\text{cell}}^{BA} \) and allows the use of AIT for periodic potentials.
X. NOBLE GAS OR CORRESPONDING ELEMENT AS BASIS FUNCTIONS?

Figure 7. The multi-electron atom: absolute error $\Delta \Delta E = |\Delta E_{SCF} - \Delta E_{AIT}|$ between unrestricted Hartree-Fock self-consistent field (SCF) energy difference $\Delta E_{SCF}$ and the AIT one, $\Delta E_{AIT}$, up to and including fifth perturbation order $p$, for $Z_A \in \{1, 2, \ldots, 8\}$ and $Z_B = Z_A + dZ$ with $dZ \in \{0.25, 0.50, \ldots, 2.00\}$. The basis functions for an initial atom $Z_A$ are in (a) each respective element $Z_A$, and in (b) one of the higher available noble gases, Xe in def2-TZVP, Kr in STO-3G, cc-pVDZ, cc-pV5Z. Using the basis functions of noble gases gains much more accuracy than increasing basis set size. Both figures show cases of diverging $\Delta E_{AIT}$ for $Z_B > 2$, while the ones from analytical computation converge (Fig. 2). Among the basis sets tested for AIT were the families of Pople, Dunning, Dunning Douglas-Kroll, Dunning JK-fitting, Ahlrichs, Lehtola, ANO and STO, all taken from Ref. 31.
XI. PERFORMANCE OF NOBLE GASES AS BASIS FUNCTIONS

The choice to use the basis functions of Xe in the basis set def2-TZVP is established by the mean average error (MAE) of the six available noble gases (Fig. 8).

![Figure 8. The multi-electron atom: mean average error (MAE) of the same transmutations as in Fig. 7 (Z_A ∈ {1, 2, ..., 8} and Z_B = Z_A + dZ with dZ ∈ {0.25, 0.50, ..., 2.00}), excluding divergent ones (1 → Z_B ∈ {2.25, 2.50, 2.75, 3.00}). First, Kr and Rn appear as more viable candidates but especially for higher Z_A, Xe prevails.](image_url)
XI. AIT’S PERFORMANCE IN MULTI-ELECTRON ATOMS FOR NON-INTEGER $Z_A, Z_B$

As a generalization of Fig. 3, we quantify the absolute error $\Delta\Delta E = \Delta E_{\text{SCF}} - \Delta E_{\text{AIT}}$ for iso-electronic interpolations where $1 \leq Z_A, Z_B \leq 10$, this time without limiting ourselves to integer nuclear charges. Again, we have used the best-performing basis set, def2-TZVP with the basis functions of Xe. Fig. 9 displays prediction errors as a heat map for all atoms $Z_A \in \{1.0, 1.1, \ldots, 10.0\}$, with $Z_B = Z_A \pm dZ$ with $dZ \in \{0.1, 0.2, \ldots, 2.0\}$. The number of electrons $N_e$ of the initial atom $Z_A$ increases in steps of $1e^-$ such that the initial atom’s overall charge $Q_A$ never exceeds $+1$ ($0 \leq Q_A = Z_A - N_e < 1$). Note the stripes of sudden increase in accuracy at integer $Z_A$ where $Q_A = 0$, whereas in between integers ($0 < Q_A < 1$), accuracy increasingly worsens, for charged initial atoms, until the next integer $Z_A$ is reached, another electron is added, and charge-neutrality is recovered ($Q_A = 0$). Here, the sensitivity to errors in the electron density becomes even more apparent than in Fig. 3 as SCF solutions between non-integer $Z_A, Z_B$ suffer the most in accuracy. Furthermore, consider the stripes’ curvature (best seen at small $Z_A$) where the errors from underestimation of densities coincide with the incipient divergence from AIT due to large $\Delta Z/Z_A$ resulting in a cancellation of errors.

![Heat Map of AIT Errors](image)

Figure 9. AIT based predictions for multi-electron atoms: Error $\Delta\Delta E = \Delta E_{\text{SCF}} - \Delta E_{\text{AIT}}$ between unrestricted Hartree-Fock SCF energy difference $\Delta E_{\text{SCF}}$ and AIT estimate $\Delta E_{\text{AIT}}$ up to and including fifth perturbation order $p$. Initial electron densities were obtained for $Z_A \in \{1.0, 1.1, \ldots, 10.0\}$, and final nuclear charges considered include $Z_B = Z_A \pm dZ$ with $dZ \in \{0.1, 0.2, \ldots, 2.0\}$.
XIII. SOFTWARE

The calculations of any self-consistent field energy or electron density are performed with the restricted/unrestricted Hartree-Fock method of PySCF\cite{27,28} for atoms with even/odd electron numbers. Further software for the purpose of data generation (i.e. math libraries, integration algorithms, numerical tools) in this letter are provided by the Python-packages NumPy\cite{39}, SciPy\cite{40}, Numba\cite{41}. Basis sets were provided via basis_set_exchange\cite{31}. Visualizations have been created using Matplotlib\cite{42}.