Relative energies without electronic perturbations via integral transform

Simon León Krug,1,2 Guido Falk von Rudorff,1,3 and O. Anatole von Lilienfeld4,5

1 University of Vienna, Computational Materials Physics, Kolingasse 14-16, 1090 Vienna, Austria
2 University of Vienna, Vienna Doctoral School in Physics, Boltzmanngasse 5, 1090 Vienna, Austria
3 Institute for Pure and Applied Mathematics (IPAM), University of California, Los Angeles, 460 Portola Plaza, Los Angeles, CA 90095, USA
4 Machine Learning Group, Technische Universität Berlin, 10587 Berlin, Germany
5 Berlin Institute for the Foundations of Learning and Data, 10587 Berlin, Germany
(Dated: May 6, 2022)

We show that the energy of a perturbed system can be fully recovered from the unperturbed electron density. We derive an alchemical integral transform by parametrizing space in terms of changes of the potential, the chain rule and integration by parts. Within the radius of convergence, the zeroth order yields the energy expansion at all orders, narrowing the textbook statement that the $p$-th order wave function derivative is necessary to describe the $(2p+1)$-th energy derivative. Results are shown for the harmonic oscillator, the hydrogen-like atom, and multi-electron atoms with up to ten electrons.

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 conceivable 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 “alchemical” changes $[1, 2]$, as introduced by E. B. Wilson already in 1962 $[3]$. Alchemical Perturbation Density Functional Theory (APDFT) $[4]$ couples the Hamiltonians of two iso-electronic systems with a mixing parameter $\lambda$ and generates approximations of relative energies as a perturbative series. For sufficiently small changes in chemical composition, this series has recently been demonstrated to converge beyond numerical precision $[5]$. By virtue of the Hellmann-Feynman theorem (cf. Eq. $1$), this perturbative expansion relies exclusively on electron density and derivatives w.r.t. $\lambda$ $[4]$. Perturbations of the electron density at any order are typically calculated explicitly (cf. Eq. $2$) via e.g. finite differences $[4, 6]$ or coupled-perturbed equations $[7-10]$, imposing significant computational cost. Recent implementations of automatic differentiation $[11]$ in numerical libraries $[12-15]$, and even in dedicated quantum chemistry software $[16-19]$, hold substantial promise to accelerate APDFT based exploration campaigns of materials compounds space $[20]$.

Here, the initial, unperturbed electron density is shown to include sufficient quantum mechanical information to recover the relative energy with respect to any isoelectronic final system – as long as the alchemical expansion converges. The calculation of density-derivatives therefore becomes unnecessary. This represents a substantial improvement over the textbook statement that the $p$-th order wave function derivative describes the $(2p+1)$-th energy derivative $[21]$. Below, we provide the derivation and its discussion, followed by numerical results. In particular, we have considered iso-electronic relative energies among hydrogen-like atoms, and among multi-electron atoms covering nuclear charges from hydrogen to neon.

The starting point of our formulation is APDFT $[4]$. 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

$$\frac{\partial E(\lambda)}{\partial \lambda} = \langle \Psi_\lambda | \hat{H}_B - \hat{H}_A | \Psi_\lambda \rangle = \int_{\mathbb{R}^3} d\mathbf{r} \Delta v(\lambda, \mathbf{r})$$

with difference in external potentials $\Delta v = v_B - v_A$. Note
that the Hellmann-Feynman theorem assumes a complete basis $|\Psi_A\rangle$, such that $\partial_t \langle \Psi_A | \langle \Psi_A | = 0$. In practice, when calculating quantum mechanical systems using (post-) Hartree-Fock methods, this is only approximately fulfilled.

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

$$\Delta E = \sum_{p=1}^{\infty} \frac{1}{p!} \int_{\mathbb{R}^3} d\lambda \Delta_\rho \left. \frac{\partial^{p-1}\rho(\lambda, \mathbf{r})}{\partial \mathbf{r}^{p-1}} \right|_{\lambda=0}$$

(2)

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

As a simplified introduction to the concept and its subsequent generalization, let us first consider the one-dimensional case (in $t$) of Eq. [2] for the first non-linear order ($p = 2$) with $v_A := v(\lambda = 0)$. Parametrizing $t \to v(\lambda)$ and using the chain rule:

$$\Delta E^{(2)} = \frac{1}{2} \int_{\mathbb{R}} dt(\lambda) \Delta t(v(\lambda)) \frac{\partial \rho(t(\lambda))}{\partial t(\lambda)} \frac{\partial t(\lambda)}{\partial \lambda} \bigg|_{\lambda=0}$$

(3)

When integrating by parts, all limit terms equal zero since the electron density vanishes at infinite distance. Inserting $\lambda = 0$ wherever possible:

$$\Delta E^{(2)} = -\frac{1}{2} \int_{\mathbb{R}} dt_A \rho_A(t_A) \frac{\partial \Delta t(t_A)}{\partial t_A} \frac{\partial t(\lambda)}{\partial \lambda} \bigg|_{\lambda=0}$$

(4)

Vide infra for our general Ansatz to explicitly state $\partial_j v|_{t=0}$ for all orders.

We now generalize this by applying Faà di Bruno’s formula (repeated chain rule) for composite functions with a vector argument [22] to obtain any derivatives of $\rho$ with respect to $\mathbf{r}(\lambda)$ and $\mathbf{r}(\lambda)$ with respect to $\lambda$. Again, all derivatives of $\rho$ with respect to $\mathbf{r}(\lambda)$ 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):

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

(5)

$$\mathcal{K}(t_A, v_A, v_B) = \sum_{p=1}^{\infty} \frac{1}{p!} \int_{\mathbb{R}^3} d\lambda \frac{\partial^{p+1}\rho(\lambda, \mathbf{r})}{\partial \mathbf{r}^{p+1}} \left. \prod_{i=1}^{p-1} \left( \sum_{\mu=1}^{3} \theta_{\mu j} \theta_{\mu k}^{p} \theta_{\mu k}^{p} \right) \right|_{\lambda=0}$$

(6)

$$\theta_{\mu j} := \frac{\partial \mu(\lambda)}{\partial \lambda} \bigg|_{\lambda=0}$$

(7)

$$S_p := \left\{ \mu_x, \mu_y, \mu_z, k_1, \ldots, k_{p-1} \right\} \ni n_0 \left\{ p - 1 = \sum_{i=1}^{p-1} i \cdot k_i, \mu_x + \mu_y + \mu_z = \sum_{i=1}^{p-1} k_i \right\}$$

(8)

Here, we denote the three spatial variables $w_A = \{ x_A, y_A, z_A \}$. The subscript $A$ is needed to discriminate between $w_A$ and the parametrization of the general coordinates $w(\lambda)$, including its derivatives $\theta_{\mu j}$ 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...
\[ \Delta E_{BA} = \int_{0}^{\infty} dr_{A} \]

Figure 1. Visualization of the Alchemical Integral Transform (AIT) for radial electron densities and kernel \( K \) corresponding to iso-electronic alchemical changes, exemplified for atoms H \( \rightarrow \) He\(^{+} \), He \( \rightarrow \) Li\(^{+} \), O \( \rightarrow \) F\(^{+} \).

at par with the coordinates, similar to the dimension of time in special relativity and reminiscent of the aforementioned four-dimensional electron density introduced by Wilson [3]. Note that the energy difference \( \Delta E \) in Eq. [5] does not depend on a general \( \rho(\lambda, r) \) or its derivatives anymore but only on the initial \( \rho_A \) and a function \( K(r, v_A, v_B) \). 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 \( \theta_{w,i} \), this heavily constraints the statement of the \((2p + 1)\)-theorem of perturbation theory: "the first \( p \) perturbative eigenfunctions are sufficient to produce the first \( 2p + 1 \) energy derivatives." [21] Now, the zeroth order \( (p = 0) \) generates all energy derivatives and hence, renders density derivatives obsolete – within the radius of convergence.

Emphasizing its alchemical characteristics and applicability for calculation of energy differences without density derivatives, we henceforth dub this method Alchemical Integral Transform (AIT) since Eq. [5] constitutes an integral transform with non-linear kernel \( K(r, v_A(r), v_B(r)) \). Assuming the parametrization \( r(\lambda) \) to be analytical on \([0, 1] \) and bijective in an environment of \( \lambda = 0 \), AIT is rigorous for iso-electronic changes. The AIT in Eq. [5] 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 \( \lambda \) [23]. Non-linear \( \lambda \)-interpolations were also already used within the context of free energy perturbation estimates relying on molecular dynamics based sampling [24]. Relative energies according to AIT are illustrated in Fig. 1 for the alchemical increase in nuclear charge of atoms.

In order to make quantitative predictions, we now propose the following Ansatz for \( \theta_{w,i} \) based on dimensional arguments,

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

where \( v_A \) and \( v_B \) correspond to the known external potentials of any pair of iso-electronic systems. From Eqs. 6 and 9 a convergence condition can be read off:

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

The general convergence behavior of the alchemical Taylor expansion is not rigorously proven except for special cases [4], but numerical evidence points towards large convergence radii of the alchemical Taylor expansion even for large changes in external potential [5], 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, on can observe the resulting divergence in the Supplemental Material (Fig. 7).

AIT and the original perturbative energy expansion match order-wise. This enables the evaluation of energy-perturbations \( \partial^p E(\lambda) \) at selected orders \( p \) and gives access to all proportional quantities, e.g., the alchemical potential \( \partial_{Z_A} E_A \) and the spatial gradient \( \partial_{R_i} E_A \) at first order \( (p = 1) \), or the alchemical hardness \( \partial^2_{Z_A} E_A \) (vide infra) and the spatial Hessian \( \partial^2_{R_i} E_A \) at second order \( (p = 2) \) [24]. Analytical higher order energy derivatives have already been presented in the context of Kohn-Sham-DFT [7].

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.

In the following, and without any loss of generality, we restrict ourselves to the case of atoms, \( v_B/v_A \to Z_B/Z_A \), which we show to be correct up to numerical precision in case of the hydrogen-like atom (cf. Fig. 2) and to be applicable to multi-electron atoms (cf. 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 \( n \):

\[
\Delta E_{\text{exact}} = -\frac{Z_B^2 - Z_A^2}{2n^2} \tag{11}
\]

The derivation and the spherically averaged electron density \( \bar{\rho}_A \) 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 with \( Z_A < Z_B \). We find the two results to agree with numerical precision \( 10^{-14} \) Ha.

Based on the energy expression, we find connections between nuclear charges and the radial expectation value of the electron density:

\[
\frac{Z_B + Z_A}{2n^2} = \sum_{p=1}^{\infty} \left( \frac{1}{p} \sum_{i=1}^{p} \frac{(-1)^{p} \cdot \mu_i!}{\prod_{i=1}^{p} k_i!} \right) \left( 1 - \frac{Z_B}{Z_A} \right)^{p-1} \times \int_0^{\infty} dr_A 4\pi r_A \bar{\rho}_A(r_A, n, Z_A) \tag{14}
\]

Figure 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 \( Z_A, Z_B \in \{1, 2, 3, 4, 5\} \), and \( Z_A < Z_B \). The numbers agree within \( 10^{-14} \) Ha. Radial electron densities for different \( n \) are shown in the inset for \( Z_a = 1 \).
and in the limit of $Z_B \rightarrow Z_A$,

$$\frac{Z_A}{4\pi n^2} = \int_0^\infty dr_A r_A \cdot \hat{p}_A(r_A, n, Z_A) = \langle \hat{p}_A \rangle_{r_A}$$

(15)

with radial expectation value $\langle \ldots \rangle_{r_A}$. This can also be derived from the analytic energy expression (cf. Supplemental Material) which confirms the equivalence in this particular case. Furthermore, the alchemical hardness $\eta_{al}$ can be obtained via the second perturbative order ($p = 2$) of Eq. [12]

$$\Delta E^{(2)}_{\text{AIT}} = \frac{1}{2} \frac{\partial^2 E_A}{\partial Z_A^2} (Z_B - Z_A)^2$$

(16)

$$= \frac{Z_B - Z_A}{2} \left(1 - \frac{Z_B}{Z_A}\right) \int_0^\infty dr_A 4\pi r_A \hat{p}_A(r_A, n, Z_A)$$

(17)

$$\Rightarrow \eta_{al} = \frac{\partial^2 E_A}{\partial Z_A^2} = \frac{4\pi}{Z_A} \langle \hat{p}_A \rangle_{r_A}$$

(18)

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 $\hat{p}_A$ 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 [26]), as shown in Refs. [4, 27]. Approaching the complete basis set limit with larger basis sets like def2-TZVP or cc-pV5Z reduces the latter error. 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 the def2–TZVP basis functions of xenon (details given in the Supplemental Material). Similar discrepancies in accuracy among basis sets for elements have also been seen before for alchemical derivatives involving noble gases [28].

Since the basis functions of chemically inert elements like noble gases are the least overfitted to the chemical behavior of the respective element, our findings suggest a strong sensitivity of $\Delta E$ to the electron density and thus to the quality of the basis set. This overfitting may bring accuracy in describing a molecule’s energy, but less so when computing a (general) system’s electron density. 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 xenon, to quantify the absolute 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 $Z_A \in \{1, 1.1, \ldots, 10.0\}$, and final nuclear charges considered include $Z_B = Z_A \pm dZ$ with $dZ \in \{0.1, 0.2, \ldots, 2.0\}$. The inset shows electron densities of the hydrogen-like atom at $Z_A = 1.9$ from the analytical solution (solid) and SCF-calculations (dashed).
mated based only on the unperturbed electron density of oxygen within $\sim 19$ and $\sim 24$ mHa, respectively. 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 due to inaccurate electron densities for charged initial atoms, until the next integer $Z_A$ is reached, another electron is added, and charge-neutrality is recovered ($Q_A = 0$). Especially close to the nucleus, $\Delta E_{AIT}$ becomes very sensitive to errors in electron density as $|K|$ becomes large (cf. Fig. [1]). This sensitivity overly shows when calculating energy differences between hydrogen-like atoms: while the approximate self-consistent field (SCF)-solution diverges for $Z_A > 2$ as the basis set has no sufficiently tight basis functions, the analytical solution holds even for $Z_A = 5$ (cf. Fig. [2]). This difference in electron densities can be seen in the inset of Fig. [3] for $Z_A = 1.9$. 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. [29]. 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 resulting in a cancellation of errors.

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 neon. As a consequence, we could show that only the initial unperturbed electron 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, narrowing the $(2p + 1)$-theorem of perturbation theory.

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 and the role of electron correlation treatment, as well as basis sets effects, might also be worthy of further attention.

ACKNOWLEDGEMENTS

We acknowledge discussions with M. Meuwly and D. Lemm, as well as support from the European Research Council (ERC-CoG Grant QML). This project has received funding from the European Union’s Horizon 2020 research and innovation programme under Grant Agreement #772834.

[1] Nicola Marzari, Stefano de Gironcoli, and Stefano Baroni. Structure and phase stability of Ga$_x$In$_{1-x}$P solid solutions from computational alchemy. Physical review letters, 72(25):4001–4004, 1994.
[2] O. Anatole von Lilienfeld, Roberto D. Lins, and Ursula Rothlisberger. Variational particle number approach for rational compound design. Phys. Rev. Lett., 95:153002, Oct 2005.
[3] E. Bright Wilson. Four-dimensional electron density function. The Journal of Chemical Physics, 36(8):2232–2233, 1962.
[4] Guido Falk von Rudorff and O. Anatole von Lilienfeld. Alchemical perturbation density functional theory. Physical Review Research, 2(2), 5 2020.
[5] Guido Falk von Rudorff. Arbitrarily precise quantum alchemy. 2021.
[6] Emily A Eikey, Alex M Maldonado, Charles D Griegor, Guido Falk von Rudorff, and John A Keith. Evaluating quantum alchemy of atoms with thermodynamic cycles: Beyond ground electronic states. The Journal of chemical physics, 156(6):064106–064106, 2022.
[7] Michal Lesiuk, Robert Balawender, and Janusz Zachara. Higher order alchemical derivatives from coupled perturbed self-consistent field theory. The Journal of Chemical Physics, 136(3):034104, 2012.
[8] Krzysztof Wolinski, James F Hinton, and Peter Pulay. Efficient implementation of the gauge-independent atomic orbital method for nmr chemical shift calculations. Journal of the American Chemical Society, 112(23):8251–8260, 1990.
[9] B I Dunlap and J Andzelm. 2nd derivatives of the local-density-functional total energy when the local potential is fitted. Physical review. A, Atomic, molecular, and optical physics, 45(1):81–87, 1992.
[10] Giorgio Domenichini and O. Anatole von Lilienfeld. Alchemical geometry relaxation. arXiv:2201.07129, 2022.
[11] Charles C. Margossian. A review of automatic differentiation and its efficient implementation. WIREs Data Mining and Knowledge Discovery, 9(4), Mar 2019.
[12] Martin Abadi, Ashish Agarwal, Paul Barham, Eugene Brevdo, Zhifeng Chen, Craig Citro, Greg S. Corrado, Andy Davis, Jeffrey Dean, Matthieu Devin, Sanjay Ghemawat, Ian Goodfellow, Andrew Harp, Geoffrey Irving, Michael Isard, Yangqing Jia, Rafal Jozefowicz, Lukasz Kaiser, Manjunath Kudlur, Josh Levenberg, Dandelion Mané, Rajat Monga, Sherry Moore, Derek Murray, Chris Olah, Mike Schuster, Jonathon Shlens, Benoit Steiner, Ilya Sutskever, Kunal Talwar, Paul Tucker, Vincent Vanhoucke, Vijay Vasudevan, Fernando Viégas, Oriol Vinyals, Pete Warden, Martin Wattenberg, Martin Wicke, Yuan Yu, and Xiaoqiang Zheng. TensorFlow: Large-scale machine learning on heterogeneous systems, 2015. Software available from tensorflow.org.

[13] Adam Paszke, Sam Gross, Soumith Chintala, Gregory Chanan, Edward Yang, Zachary DeVito, Zeming Lin, Alban Desmaison, Luca Antiga, and Adam Lerer. Automatic differentiation in pytorch. 2017.

[14] Jesper Sören Drämsch and Contributors. Complex-valued neural networks in keras with tensorflow, 2019.

[15] Theano Development Team. Theano: A Python framework for fast computation of mathematical expressions. arXiv e-prints, abs/1605.02688, May 2016.

[16] Teresa Tamayo-Mendoza, Christoph Kreisbeck, Roland Lindh, and Álan Aspuru-Guzik. Automatic differentiation in quantum chemistry with applications to fully variational hartree–fock. ACS central science, 4(5):559–566, 2018.

[17] Ville Bergholm, Josh Izaac, Maria Schuld, Christian Gogolin, M. Sohaib Alam, Shahnawaz Ahmed, Juan Miguel Arrazola, Carsten Blank, Alain Delgado, Soran Jahangiri, Keri Mc Kiernan, Johannes Jakob Meyer, Zeyue Niu, Antal Száva, and Nathan Killoran. PennyLane: Automatic differentiation in hybrid quantum-classical computations. arXiv:1811.04968, 2018.

[18] Juan Miguel Arrazola, Soran Jahangiri, Alain Delgado, Jack Ceroni, Josh Izaac, Antal Száva, Utkarsh Azad, Robert A. Lang, Zeyue Niu, Olivia Di Matteo, Romain Moyard, Jay Soni, Maria Schulz, Rodrigo A. Vargas-Hernández, Teresa Tamayo-Mendoza, Cedric Yen-Yu Lin, Álan Aspuru-Guzik, and Nathan Killoran. Differentiable quantum computational chemistry with pennylane. arXiv:2111.09967, 2021.

[19] Muhammad F Kasim, Susi Lehtola, and Sam M Vinko. Dqc: A python program package for differentiable quantum chemistry. The journal of chemical physics, 156(8):084801–084801, 2022.

[20] Gerbrand Ceder. Predicting properties from scratch. Science, 280(5366):1099–1100, 1998.

[21] X. Gonze and J.-P. Vigneron. Density-functional approach to nonlinear-response coefficients of solids. Phys. Rev. B, 39:13120–13128, Jun 1989.

[22] Rumen L. Mishkov. Generalization of the formula of faa di bruno for a composite function with a vector argument. International Journal of Mathematical and Mathematical Sciences, 24(7):481–491, 2000.

[23] O. Anatole von Lilienfeld. Accurate ab initio energy gradients in chemical compound space. The Journal of chemical physics, 131(16):164102–164102–6, 2009.

[24] P. E. Smith and W. F. van Gunsteren. Predictions of free energy differences from a single simulation of the initial state. JCP, 100:577, 1994.

[25] O. Anatole von Lilienfeld and Mark E. Tuckerman. Molecular grand-canonical ensemble density functional theory and exploration of chemical space. The Journal of Chemical Physics, 125(15):154104, 2006.

[26] Peter Pulay. Ab initio calculation of force constants and equilibrium geometries in polyatomic molecules. i. theory. Molecular physics, 100(1):57–62, 2002.

[27] Giorgio Domenichini, Guido Falk von Rudorff, and O. Anatole von Lilienfeld. Effects of perturbation order and basis set on alchemical predictions. The Journal of chemical physics, 153(14):144118–144118, 2020.

[28] Robert Balawender, Michael Lesiuk, Frank De Proft, Christian Van Alsenoy, and Paul Geertings. Exploring chemical space with alchemical derivatives: alchemical transformations of H through Ar and their ions as a proof of concept. Physical Chemistry Chemical Physics (Incorporating Faraday Transactions), 21(43):23865–23879, November 2019.

[29] Maximilian A Ambroise and Frank Jensen. Probing basis set requirements for calculating core ionization and core excitation spectroscopy by the delta self-consistent-field approach. Journal of chemical theory and computation, 15(1):325–337, 2019.

[30] Claude Cohen-Tannoudji, Bernard Diu, and Franck Lalooë. Quantenmechanik, Band 2. Walter de Gruyter GmbH & Co KG, 2008.

[31] Wolfram research, inc., wolframalpha knowledgebase, champaign, 2021.

[32] J. P DAHL and M SPRINGBORG. The morse oscillator in position space, momentum space, and phase space. The Journal of chemical physics, 88(7):4535–4547, 1988.

[33] Qiming Sun, Timothy C. Berkelbach, Nick S. Blunt, George H. Booth, Sheng Guo, Zhendong Li, Junzi Liu, James D. McClain, Elvira R. Sayfutyarova, Sandeep Sharma, Sebastien Wouters, and Garnet Kin-Lic Chan. Pyscf: the python-based simulations of chemistry framework. WIREs Computational Molecular Science, 8(1):e1340, 2018.

[34] Qiming Sun, Xing Zhang, Samragni Banerjee, Peng Bao, Marc Barby, Nick S. Blunt, Nikolay A. Bogdanov, George H. Booth, Jia Chen, Zhi-Hao Cui, Janus J. Eriksson, Yang Gao, Sheng Guo, Jan Hermann, Matthew R. Hermes, Kevin Koh, Peter Koval, Susi Lehtola, Zhen-dong Li, Junzi Liu, Nare Mardirossian, James D. McClain, Mario Motta, Bastien Mussard, Hung Q. Pham, Artem Pulkin, Wirawan Purwanto, Paul J. Robinson, Enrico Ronca, Elvira R. Sayfutyarova, Maximilian Scheurer,
Henry F. Schurkus, James E. T. Smith, Chong Sun, Shining Sun, Shiv Upadhyay, Lucas K. Wagner, Xiao Wang, Alec White, James Daniel Whitfield, Mark J. Williamson, Sebastian Wouters, Jun Yang, Jason M. Yu, Tianyu Zhu, Timothy C. Berkelbach, Sandeep Sharma, Alexander Yu. Sokolov, and Garnet Kin-Lic Chan. Recent developments in the pyscf program package. *The Journal of Chemical Physics*, 153(2):024109, 2020.

[35] Charles R. Harris, K. Jarrod Millman, Stéfan J. van der Walt, Ralf Gommers, Pauli Virtanen, David Cournapeau, Eric Wieser, Julian Taylor, Sebastian Berg, Nathaniel J. Smith, Robert Kern, Matti Picus, Stephan Hoyer, Marten H. van Kerkwijk, Matthew Brett, Allan Haldane, Jaime Fernández del Río, Mark Wiebe, Pearu Peterson, Pierre Gérard-Marchant, Kevin Sheppard, Tyler Reddy, Warren Weckesser, Hameer Abbasi, Christoph Gohlke, and Travis E. Oliphant. Array programming with NumPy. *Nature*, 585(7825):357–362, September 2020.

[36] Pauli Virtanen, Ralf Gommers, Travis E. Oliphant, Matt Haberland, Tyler Reddy, David Cournapeau, Evgeni Burovski, Pearu Peterson, Warren Weckesser, Jonathan Bright, Stéfan J. van der Walt, Matthew Brett, Joshua Wilson, K. Jarrod Millman, Nikolay Mayorov, Andrew R. J. Nelson, Eric Jones, Robert Kern, Eric Larson, C J Carey, Ilhan Polat, Yu Feng, Eric W. Moore, Jake VanderPlas, Denis Laxalde, Josef Perktold, Robert Cimrman, Ian Henriksen, E. A. Quintero, Charles R. Harris, Anne M. Archibald, Antônio H. Ribeiro, Fabian Pedregosa, Paul van Mulbregt, and SciPy 1.0 Contributors. SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nature Methods*, 17:261–272, 2020.

[37] Siu Kwan Lam, Antoine Pitrou, and Stanley Seibert. Numba: A llvm-based python jit compiler. In *Proceedings of the Second Workshop on the LLVM Compiler Infrastructure in HPC*, LLVM ’15, New York, NY, USA, 2015. Association for Computing Machinery.

[38] Benjamin P. Pritchard, Doaa Altarawy, Brett Didier, Tara D. Gibson, and Theresa L. Windus. New basis set exchange: An open, up-to-date resource for the molecular sciences community. *Journal of Chemical Information and Modeling*, 59(11):4814–4820, Nov 2019.

[39] J. D. Hunter. Matplotlib: A 2d graphics environment. *Computing in Science & Engineering*, 9(3):90–95, 2007.
DERIVATION OF Eqs. 5 AND 6

Starting with Eq. 2, we shift the index \( p \rightarrow p + 1: \)

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

We want to reshape this expression and do so by transferring the \( \lambda \)-dependency of the general \( \rho(\lambda, r) \) to a parametrization of the coordinates \( r \rightarrow r(\lambda) \) where \( r(\lambda = 0) = r_A \). In addition, we demand the parametrization to be analytic at \( \lambda = 0 \) and invertible around \( \lambda = 0 \), with the inverse denoted as \( r^{-1}: \mathbb{R}^3 \rightarrow [0, 1] \). Hence, we can rewrite:

\[
\rho(\lambda, r) \rightarrow \rho(\lambda, r(\lambda)) = \rho(r^{-1}(r(\lambda)), r(\lambda)) =: \tilde{\rho}(r(\lambda)) \quad (20)
\]

Every \( r \) in Eq. 19 shall now be transformed as \( r \rightarrow r(\lambda): \)

\[
\Delta E = \sum_{p=0}^{\infty} \frac{1}{(p+1)!} \int_{\mathbb{R}^3} dr(\lambda) \Delta v(r(\lambda)) \frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial \lambda^p} \bigg|_{\lambda=0} \quad (21)
\]

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) [22]:

\[
\frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial \lambda^p} = \sum_{0 \leq q_1 \leq p} \frac{p!}{q_1! (q_1)!} \left( \frac{\partial \tilde{\rho}(r(\lambda))}{\partial x(\lambda)} \right)^{q_1} \left( \frac{\partial x(\lambda)}{\partial \lambda} \right)^{q_1} \left( \frac{\partial \tilde{\rho}(r(\lambda))}{\partial y(\lambda)} \right)^{q_1} \left( \frac{\partial y(\lambda)}{\partial \lambda} \right)^{q_1} \left( \frac{\partial \tilde{\rho}(r(\lambda))}{\partial z(\lambda)} \right)^{q_1} \left( \frac{\partial z(\lambda)}{\partial \lambda} \right)^{q_1} \bigg|_{\lambda=0} \quad (22)
\]
The sums run over all non-negative integer solutions of the following \( p + 1 \) linear Diophantine equations:

\[
\sum_0^n: \quad k_0 + 2k_2 + \cdots + pk_p = p \tag{23}
\]

\[
\sum_1^n: \quad q_1^x + q_1^y + q_1^z = k_1 \tag{24}
\]

\[
\vdots
\]

\[
\sum_p^n: \quad q_p^x + q_p^y + q_p^z = k_p \tag{25}
\]

Furthermore, the conditions hold:

\[
\mu_x = q_1^x + \cdots + q_p^x \tag{26}
\]

\[
\mu_y = q_1^y + \cdots + q_p^y \tag{27}
\]

\[
\mu_z = q_1^z + \cdots + q_p^z \tag{28}
\]

\[
k = \mu_x + \mu_y + \mu_z = k_1 + \cdots + k_p \tag{29}
\]

Note that this only holds for the first and higher derivatives. In case of \( p = 0 \), the sum \( \sum_0^n \) shall be taken over all \( \mu_x + \mu_y + \mu_z = 0 \) which nicely reproduces the result of Eq. \( \text{[2]} \) for \( p = 0 \).

The chain of \( \tilde{\rho} \) 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:

\[
\Delta E = \sum_{p=0}^{\infty} \frac{1}{p+1} \int_{R^3} dr(\lambda) \Delta v(r(\lambda)) \sum_0^n \frac{1}{\prod_{i=1}^p (q_i^x)! \, k_i!} \left( \frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial x^i \partial y^j \partial z^k} \right) \left( \frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial x^i \partial y^j \partial z^k} \right) \left( \frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial x^i \partial y^j \partial z^k} \right) \bigg|_{\lambda=0} \tag{30}
\]

Secondly, we apply the multinomial theorem:

\[
\Delta E = \sum_{p=0}^{\infty} \frac{1}{p+1} \sum_0^n \frac{1}{\prod_{i=1}^p (q_i^x)! \, k_i!} \int_{R^3} dr(\lambda) \Delta v(r(\lambda)) \left( \frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial x^i \partial y^j \partial z^k} \right) \left( \frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial x^i \partial y^j \partial z^k} \right) \left( \frac{\partial^p \tilde{\rho}(r(\lambda))}{\partial x^i \partial y^j \partial z^k} \right) \bigg|_{\lambda=0} \tag{31}
\]
Within the brackets, only $\Delta \vartheta(r(\lambda))$ is non-constant w.r.t. $x(\lambda), y(\lambda), z(\lambda)$ because:

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

As $\partial_{x}[x + y + z] = 1$, already the first derivative w.r.t $\lambda$ vanishes. The same goes for $y$ and $z$. Set $\lambda = 0$ wherever possible, revert the index shift from the beginning ($p \to p - 1$) and use $k = \mu_{x} + \mu_{y} + \mu_{z}$:

$$
\Delta E = \int_{\mathbb{R}^{3}} dr_{A} \rho_{A}(r_{A}) \mathcal{K}(r_{A}, v_{A}, v_{B})
$$

$$
\mathcal{K}(r_{A}, v_{A}, v_{B}) = \sum_{p=1}^{\infty} \frac{1}{p} \sum_{S_{p}} \prod_{i=1}^{p-1} \left( \sum_{\omega \in \{x, y, z\}} \theta_{\omega,i} \right)^{k_{i}}
$$

$$
\theta_{\omega,i} := - \frac{1}{i!} \left. \frac{\partial \vartheta(\lambda)}{\partial x_{i}} \right|_{\lambda=0}
$$

$$
S_{p} := \left\{ \mu_{x}, \mu_{y}, \mu_{z}, k_{1}, \ldots, k_{p-1} \in \mathbb{N}_{0} \mid p - 1 = \sum_{i=1}^{p-1} i \cdot k_{i}, \mu_{x} + \mu_{y} + \mu_{z} = \sum_{i=1}^{p} k_{i} \right\}
$$

Eqs. [19] and [34] match order-wise. This is to be expected as the derivation leaves the sum over $p$ untouched.
SOLUTIONS TO THE LINEAR DIOPHANTINE EQUATIONS

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

\[
p \left[ \mu_1, \mu_2, \mu_3, k_1, \ldots, k_{p+1} \right]
\]

\[
\begin{array}{c}
1 [0,0,0] \\
2 1[1,0,0,1],[0,1,0,1],[0,0,1,1] \\
3 0,0,1,0,1,[0,0,2,2,0],[0,1,0,0,1],[0,1,2,0],[0,2,0,2,0],[1,0,0,0,1],[1,0,1,0],[1,1,0,2,0],[2,0,0,2,0] \\
4 0,0,1,0,0,1,[0,0,2,1,1,0],[0,0,3,3,0,0],[0,1,0,0,0,1],[0,1,1,1,1,0],[0,1,2,3,0,0],[0,2,0,1,1,0],[0,2,1,3,0,0],
[0,3,0,3,0,0],[1,0,0,0,0,1],[1,0,1,1,1,0],[1,0,2,3,0,0],[1,1,0,1,1,0],[1,1,1,3,0,0],[1,2,0,3,0,0],[2,0,0,1,1,0],
[2,0,1,3,0,0],[2,1,0,3,0,0],[3,0,0,3,0,0] \\
5 0,0,1,0,0,0,1,[0,0,2,0,0,0,1],[0,0,2,1,0,1,0],[0,0,3,2,1,0,0],[0,0,4,4,0,0,0],[0,1,0,0,0,0,1],[0,1,1,0,2,0,0],
[0,1,1,1,1,0,1],[0,1,2,1,1,0,1],[0,1,3,4,0,0,0],[0,2,0,0,2,0,0],[0,2,0,1,2,0,0],[0,2,1,1,2,0,0],[0,2,2,4,0,0,0],
[0,3,0,2,1,0,0],[0,3,1,4,0,0,1],[0,4,0,4,0,0,0],[1,0,0,0,0,0,1],[1,0,1,0,2,0,0],[1,0,1,1,1,0,1],[1,0,2,2,1,0,0],
[1,0,3,4,0,0,0],[1,1,0,0,2,0,0],[1,1,0,1,1,1,0],[1,1,2,1,1,0,0],[1,1,2,4,0,0,0],[1,2,0,2,1,0,0],[1,2,1,4,0,0,0],
[1,3,0,4,0,0,0],[2,0,0,1,2,0,0],[2,0,1,1,2,0,0],[2,0,2,4,0,0,0],[2,1,0,2,1,0,0],[2,1,1,4,0,0,0],
[2,2,0,4,0,0,0],[3,0,0,2,1,0,0],[3,0,1,4,0,0,0],[3,1,0,4,0,0,0],[4,0,0,4,0,0,0] \\
6 0,1,0,0,0,0,1,[0,0,2,0,1,1,0],[0,0,2,0,1,0,1],[0,0,3,1,2,0,0,0],[0,0,3,2,0,1,0,0],[0,0,4,3,1,0,0,0],
[0,0,5,5,0,0,0,0],[0,1,0,0,0,0,0,1],[0,1,1,0,1,1,0],[0,1,1,1,0,0,0,1],[0,1,2,1,2,0,0,0],[0,1,2,2,0,1,0,0],
[0,1,3,3,0,0,0,0],[0,1,4,5,0,0,0,0],[0,2,0,0,1,1,0],[0,2,0,0,1,1,0],[0,2,0,0,1,1,0],[0,2,0,1,2,0,0,0],[0,2,1,2,0,1,0,0],
[0,2,3,1,0,0,0],[0,2,3,5,0,0,0,0],[0,3,0,1,2,0,0,0],[0,3,0,2,0,1,0,0],[0,3,1,3,1,0,0,0],[0,3,2,5,0,0,0,0],
[0,4,0,3,1,0,0],[0,4,1,5,0,0,0,0],[0,5,0,5,0,0,0,0],[1,0,0,0,0,0,0,1],[1,0,1,0,1,1,0],[1,0,1,0,1,1,0],[1,0,1,0,1,1,0],
[1,0,2,1,2,0,0,0],[1,0,2,2,0,1,0,0],[1,0,3,3,1,0,0],[1,0,4,5,0,0,0,0],[1,1,0,0,1,1,0],[1,1,0,1,0,1,0],[1,1,0,1,0,1,0],
[1,1,1,1,2,0,0,0],[1,1,1,2,0,1,0,0],[1,1,2,3,1,0,0],[1,1,3,5,0,0,0,0],[1,2,0,1,2,0,0,0],[1,2,0,2,0,1,0,0],
[1,2,1,3,0,0,0],[1,2,2,5,0,0,0,0],[1,3,0,3,1,0,0],[1,3,1,5,0,0,0,0],[1,4,0,5,0,0,0,0],[2,0,0,0,1,1,0,0],
[2,0,0,1,0,0,1,0],[2,0,1,1,2,0,0,0],[2,0,1,2,0,1,0,0],[2,0,2,3,1,0,0,0],[2,0,3,5,0,0,0,0],[2,1,0,1,2,0,0,0],
[2,1,0,2,1,0,0,0],[2,1,1,3,0,0,0],[2,1,2,5,0,0,0,0],[2,2,0,3,1,0,0,0],[2,2,1,5,0,0,0,0],[2,3,0,5,0,0,0,0],
[3,0,0,1,2,0,0,0],[3,0,0,2,0,1,0,0],[3,0,1,3,1,0,0,0],[3,0,2,5,0,0,0,0],[3,1,0,3,1,0,0,0],[3,1,1,5,0,0,0,0],
[3,2,0,5,0,0,0,0],[4,0,0,3,1,0,0,0],[4,0,1,5,0,0,0,0],[4,1,0,5,0,0,0,0],[5,0,0,5,0,0,0,0]
\end{array}
\]

ELECTRON DENSITY OF HYDROGEN-LIKE ATOM

The solutions of the hydrogen-like atom with nuclear charge \(Z_A\) in spherical coordinates and atomic units are [30]:

\[
\Psi_{nm\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{m\ell}(\theta, \phi)
\]

\[
R_{n\ell}(r) = -\left( \frac{2Z_A}{n} \right)^{3/2} \left( \frac{2Z_A r}{n} \right)^l L_{n-l}^{(2l+1)} \left( \frac{2Z_A r}{n} \right) \sqrt{\frac{(n-l-1)!}{2n(n+l)!}} \exp \left( -\frac{Z_A r}{n} \right)
\]

with the radial contribution \(R_{n\ell}\), associated Laguerre polynomials \(L\) and the spherical harmonics \(Y_{m\ell}\). We neglected the change of the reduced mass \(\mu\) with increasing nuclear mass and chose \(\mu \approx m_e\), hence \(\alpha_\mu \approx \alpha_0 = 1\). The spherically averaged electron density \(\bar{\rho}_A\), depending only on \(r, n\) and \(Z_A\), is then given by:

\[
\bar{\rho}_A(r_A, n, Z_A) = \frac{1}{2n-1} \sum_{l=-n+1}^{n+1} \frac{1}{4\pi} \left( \frac{2Z_A}{n} \right)^3 \left( \frac{2Z_A r_A}{n} \right)^{2l} \left( \frac{L_{n-l}^{(2l+1)}}{n} \right)^2 \left( \frac{(n-l-1)!}{2n(n+l)!} \right) \exp \left( -\frac{Z_A r_A}{n} \right)
\]
DERIVATION OF EQ. [12]

A simplification for radially symmetric systems can be derived from Eqs. [3] and [6] 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. [22] 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:

\[
\Delta E_{\text{AIT}} = \int_0^\infty dr_A r_A^2 \int d\Omega \rho_A(r_A, n, Z_A) \sum_{p=1}^\infty \frac{1 - Z_A}{Z_A} \sum_{l_p} \left[ \frac{\partial^{\mu_l} - Z_B + Z_A}{\partial r_A} \right] \prod_{i=1}^{p-1} \frac{r_A}{k_i!} \tag{42}
\]

\[
= \int_0^\infty dr_A 4\pi r_A \tilde{\rho}_A(r_A, n, Z_A) \sum_{p=1}^\infty \left\{ \frac{1}{p} \prod_{l_p} \frac{(-1)^{\mu_l} \cdot \mu_l!}{\prod_{i=1}^{p-1} k_i!} \right\} (-Z_B + Z_A) \left( 1 - \frac{Z_B}{Z_A} \right)^{p-1} \tag{43}
\]

\[
T_p := \left\{ \mu_r, k_1, \ldots, k_{p-1} \in \mathbb{N}_0 \mid p - 1 = \sum_{i=1}^{p-1} i \cdot k_i, \mu_r = \sum_{i=1}^{p-1} k_i \right\} \tag{44}
\]

The first few \( g_p \) are:

\[
\begin{array}{cccccccc}
p & 1 & 2 & 3 & 4 & 5 & 6 & \ldots \\
g_p & 1 & -\frac{1}{2} & -\frac{1}{6} & -\frac{1}{24} & -\frac{1}{120} & -\frac{1}{720} & \ldots \\
\end{array}
\]

PROOF OF EQ. [15]

Eq. [15] is visualized in Fig. 4. However, it can also be proven with the following orthogonality relation of the Laguerre polynomials [31]:

\[
\int_0^\infty dx \ e^{-x} x^k L_{(m)}^{(k)}(x) L_{(n)}^{(k)}(x) = \frac{(n + k)!}{n!} \delta_{mn} \tag{45}
\]

Thus, we can write:

\[
\frac{Z_A}{4\pi n^2} = \int_0^\infty dr_A r_A \tilde{\rho}_A(r_A, n, Z_A) \tag{46}
\]

\[
= \frac{1}{2n - 1} \sum_{l=-(n-1)}^{+(n-1)} \frac{1}{4\pi} \left( \frac{2Z_A}{n} \right)^3 \frac{(n - l - 1)!}{2m(n + l)!} \int_0^\infty dr_A r_A \left( \frac{2Z_A r_A}{n} \right)^{2l} \left( L_{(n-l-1)}^{(2l+1)} \left( \frac{2Z_A r_A}{n} \right) \right)^2 \exp \left( -\frac{2Z_A r_A}{n} \right) \tag{47}
\]

Substitute \( \nu = 2Z_A r_A / n \):

\[
= \frac{1}{2n - 1} \sum_{l=-(n-1)}^{+(n-1)} \frac{Z_A}{4\pi n^2} \frac{(n - l - 1)!}{(n + l)!} \int_0^\infty d\nu \ e^{-\nu} \nu^{2l+1} \left( L_{(n-l-1)}^{(2l+1)}(\nu) \right)^2 \tag{48}
\]

\[
= \frac{Z_A}{4\pi n^2}
\]
Figure 4. The hydrogen-like atom: \( Z_A/4\pi n^2 \) versus radial expectation value of the electron density \( \langle \hat{\rho}_A(r_A) \rangle_{r_A} \) at different principal quantum numbers \( n \) for \( Z_A \in \{1, 2, 3, 4, 5\} \). The numbers match up to \( 10^{-16} \) Ha

THE DIRAC DELTA POTENTIAL

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

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

with energy eigenvalue and wave functions

\[
E = \frac{-b^2}{2} , \quad \Psi(x) = \sqrt{b} \cdot \exp(-b|x|) .
\]

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

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

\[
= \int_{-\infty}^{\infty} dx_A b_A \cdot \exp(-2b_A|x_A|) \sum_{p=1}^{\infty} \frac{\left(1 - \frac{b_A}{b_B}\right)^{p-1}}{p} \sum_{T_p} (b_A - b_B) \frac{\partial^p \delta(x_A)}{\partial x_A^{\mu_1}} \left[ \prod_{i=1}^{p-1} \frac{x_A^{k_i}}{k_i!} \right]
\]

\[
= b_A^2 \sum_{p=1}^{\infty} \frac{\left(1 - \frac{b_A}{b_B}\right)^{p}}{p} \sum_{T_p} \left[ \prod_{i=1}^{p-1} \frac{1}{k_i!} \right] \int_{-\infty}^{\infty} dx_A \exp(-2b_A|x_A|) x_A^{\mu_1} \frac{\partial^p \delta(x_A)}{\partial x_A^{\mu_1}}
\]

with \( T_p \) same as in Eq. [44]
The integral can be evaluated by applying the distributional derivative of the Dirac delta function:

\[
= b_A^2 \sum_{p=1}^{\infty} \left( 1 - \frac{b_B}{b_A} \right)^p \sum_{p=1}^{\mu} \left[ \prod_{k=1}^{p-1} \frac{1}{\mu_k} \right] \mu_k! (-1)^{\mu_k}
\]

where \( g_p \) same as in Eq. 43. Similar to the hydrogen-like atom, one can numerically show:

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

Finally, we obtain the energy difference from AIT:

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

This is identical to the energy difference calculated from Eq. 50.

**THE QUANTUM HARMONIC OSCILLATOR**

Consider the potential of the one-dimensional harmonic oscillator

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

with energy eigenvalue and wave functions

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

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

where \( H_n \) are the physicist’s Hermite polynomials [30].

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 \( \Lambda_{reg} \gg \Delta E_{BA} \) 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. 62 and 63 equal one another with small numerical error as seen in Fig. 6a.

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

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

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

$$v(x) = D \cdot (\exp(-2a \cdot (x - x_0)) - 2 \exp(-a \cdot (x - x_0))) \quad D, a > 0$$ \hspace{1cm} (64)

with energy eigenvalue and wave functions

$$E_n = \sqrt{2} D a \cdot \left(n + \frac{1}{2}\right) \cdot \left(1 - \frac{a}{2 \sqrt{2D}} \left(n + \frac{1}{2}\right)\right) - D$$ \hspace{1cm} (65)

$$\Psi_n(x) = N(z, n) \sqrt{a} \xi^{z-n-1/2} e^{-\xi/2} L_n^{(2z-2n-1)}(\xi)$$ \hspace{1cm} (66)

$$z = \frac{2D}{a}$$ \hspace{1cm} (67)

$$\xi = 2z \cdot e^{-a(x-x_0)}$$ \hspace{1cm} (68)

$$N(z, n) = \sqrt{\frac{(2z - 2n - 1)\Gamma(n + 1)}{\Gamma(2z - n)}}$$ \hspace{1cm} (69)

where $L$ are the associated 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 to 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 $D_A = 15$, $a_A = 1$, $x_{0,A} = 0$ 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 $\Delta E_{\text{AI}}$ up to and including fifth perturbation order $p$, below the error $\Delta \Delta E = |\Delta E_{\text{exact}} - \Delta E_{\text{AI}}|$, for different quantum numbers $n$. In (a), the quantum harmonic oscillator with $\omega_A, \omega_B \in \{1.0, 1.2, \ldots, 1.2\}$ and $\omega_A < \omega_B$. In (b), the Morse potential centered at $x_0 = 0$ with $a_A = a_B = 1, D_A = 22, D_B = D_A - dZ$ and $dZ \in \{0.1, 0.2, \ldots, 1.0\}$. 
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 $v_{\text{cell}}$:

$$v_{A,B}(r) = \sum_{j_1=0}^{N_1-1} \cdots \sum_{j_n=0}^{N_n-1} v_{\text{cell}}(r_1 + j_1 \cdot R_1, \ldots, r_n + j_n \cdot R_n)$$  \hspace{1cm} (70)

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:

$$\Delta E_{BA} = \int_{\mathbb{R}^n} d\mathbf{r} \rho_A(\mathbf{r}_A) \ K(\mathbf{r}_A, v_A, v_B)$$  \hspace{1cm} (71)

$$\Leftrightarrow [N_1 N_2 \ldots N_n] \Delta E_{\text{cell}}^{BA} = [N_1 N_2 \ldots N_n] \int_{\Omega} d\mathbf{r} \rho_A(\mathbf{r}_A) \ K(\mathbf{r}_A, v_{\text{eff}}_A, v_{\text{eff}}_B)$$  \hspace{1cm} (72)

Dropping the factors of $N_1 N_2 \ldots N_n$ on both sides allows the use of AIT for periodic potentials.
Figure 7. The multi-electron atom: absolute error $\Delta E = |\Delta E_{\text{SCF}} - \Delta E_{\text{AIT}}|$ between unrestricted Hartree-Fock self-consistent field (SCF) energy difference $\Delta E_{\text{SCF}}$ and the AIT one, $\Delta E_{\text{AIT}}$, 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 $\Delta E_{\text{AIT}}$ ($Z_A = 1 \rightarrow Z_B \in \{2.25, 2.50, 2.75, 3.00\}$). Note that the energy differences from SCF-calculations in the hydrogen-like atom diverge for $Z_B > 2$, while the ones from analytical computation converge (Fig. [5]).
PERFORMANCE OF NOBLE GASES AS BASIS FUNCTIONS

The choice to use the basis functions of xenon 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 (\(Z_A \in \{1, 2, \ldots, 8\}\) and \(Z_B = Z_A + dZ\) with \(dZ \in \{0.25, 0.50, \ldots, 2.00\}\), excluding divergent ones (1 → \(Z_B \in \{2.25, 2.50, 2.75, 3.00\}\)). First, Kr and Rn appear as more viable candidates but especially for higher \(Z_A\), Xe prevails.

SOFTWARE

The calculations of any self-consistent field energy or electron density are performed with the unrestricted Hartree-Fock method of PySCF [33, 34]. 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 [35], SciPy [36], Numba [37]. Basis sets were provided via basis_set_exchange [38]. Visualizations have been created using Matplotlib [39].