# Linear Response Methods in Quantum Chemistry

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**Abstract**   Linear response methods allow for the calculation of various observables connected to the electronic response to an external perturbation. In this chapter, we give an introduction to density functional perturbation theory (DFPT) and several of its applications. After a general derivation of the central DFPT equations we explicitly discuss the calculation of nuclear magnetic resonance (NMR) chemical shifts for the determination of supramolecular packing motifs. In the last part of our chapter, we outline an approach to the calculation of van der Waals interactions from first principles using DFPT.

## 1 Introduction

Density functional theory (DFT) [12, 14] represents the ground state of an electronic system by its electronic density, from which all ground state properties can then be calculated. In the Kohn–Sham(KS) formulation, the electronic many-body problem is broken down to non-interacting single-electron wave functions in the effective potential of the remaining system,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - v_{eff}\right)\varphi_i = \varepsilon_i\varphi_i. \tag{1}$$

DFT has proven itself to be a powerful tool which has been widely used to investigate systems of physical, chemical and biological importance with the structure ranging from single atoms and molecules to condensed phase systems and from crystalline to amorphous structures.

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Many experimentally observable properties do not depend on the ground state of the system alone, but correspond to a reaction of the system to external influences, resulting in an excitation of the system. The direct computation of excited state properties within the framework of DFT can be achieved using time-dependent DFT (TDDFT, see also Chap. "Time-dependent Density Functional Theory" by Doltsinis). For many spectroscopic observables however, it is possible to use an alternative route for the calculation. These properties then are related to second or third derivatives of the total energy of the system, which can be calculated in a finite-differences approach. This is achieved by minimally modifying, e.g., the atomic positions or external field to retrieve the changes in energy. This method has the advantage of a straightforward implementation, but its results often strongly depend on the chosen parameters of the finite variation.

Another possibility to calculate these spectroscopic properties is the direct perturbative calculation of the systems response to an infinitesimally small external perturbation. In DFT this is achieved within the framework of density functional perturbation theory.

Vibrational properties for example depend on the second derivate of the total energy with respect to the atomic coordinates

$$\frac{\partial^2 \mathscr{E}_{KS}}{\partial \mathbf{R}_a \partial \mathbf{R}_b}, \tag{2}$$

which build the components of the Hessian matrix, whose eigenvalues and eigenvectors are directly connected to the frequencies and modes of the harmonic vibration.

The static polarizability, on the other hand, is the second derivate with respect to an external electric field:

$$\frac{\partial^2 \mathscr{E}_{KS}}{\partial E_a \partial E_b}. \tag{3}$$

For an explicitly time-dependent electric field, such as the field of a laser beam, the polarizability becomes frequency dependent. This frequency dependent polarizability is a necessary input to obtain the van der Waals interaction, which is missing in conventional DFT approaches [see Chap. "Quantum Cluster Equilibrium"].

The NMR shielding tensor is related to the energy derivative with respect to the magnetic moment and an external magnetic field:

$$\frac{\partial^2 \mathscr{E}_{KS}}{\partial m_a \partial B_b}. \tag{4}$$

In the NMR Sect. 3, the specific implementation details of this formulation are discussed in detail.

## 2 Density Functional Perturbation Theory

The theoretical concept of DFPT is based on the variational principle applied to a perturbed system. In case of an unperturbed system in its electronic ground state, the variational principle states that the ground state KS-orbitals are those which minimize the KS-energy. In presence of a perturbation, the electronic structure will adjust in such a way that the perturbed energy is again minimized. This property is used to calculate the perturbed states by a variational approach [2, 7, 8].

In the unperturbed ground state, the standard Kohn–Sham functional is given by

$$\mathcal{E}_{KS}[\{\phi_o\}] = \sum_o f_o \langle \phi_o| - \tfrac{1}{2}\nabla^2|\phi_o\rangle + \int (V_{ext} + V_H)(\mathbf{r})n(\mathbf{r})d^3r + \mathcal{E}_{xc}[n] \quad (5)$$

where the sum runs over the $N$ doubly ($f_o = 2$) occupied states with $o \in \{1, \ldots, N\}$ and the electronic density is given by

$$n(\mathbf{r}) = \sum_o f_o |\phi_o(\mathbf{r})|^2. \quad (6)$$

In presence of a small perturbation, the response of any property represented by an observable $X$ can in general be obtained to arbitrary order by a perturbative expansion around its unperturbed value $X^{(0)}$ according to

$$X = \sum_n \lambda^n X^{(n)}, \quad (7)$$

with

$$X^{(n)} = \frac{1}{n!}\frac{d^n X}{d\lambda^n}. \quad (8)$$

Common quantities for $X$ are the energy $E$, the KS-orbitals $|\phi_o\rangle$, or the density $n$. The perturbation parameter $\lambda$ is an infinitesimally small auxiliary variable which helps to separate different orders of the response with respect to the perturbation and do not occur in the final expressions.

The presence of the perturbation is represented by an additional linearized energy term in the total energy functional

$$\mathcal{E}^{tot}[\{\phi_o\}] = \mathcal{E}^{KS}[\{\phi_o\}] + \lambda\mathcal{E}^{pert}[\{\phi_o\}], \quad (9)$$

with the ensemble of occupied KS orbitals $\{\phi_o\}$ which represent a single-determinant wave function.

In principle, this equation can be solved for a finite perturbation strength $\lambda$ with the standard ground state variational approach. The results of this *finite-difference* approach, however, show dependencies on the choice of the perturbation strength, and possibly induced symmetry breaking increases the computational costs.

Instead, the more common alternative route is an analytical separation of the different orders of the perturbation and their explicit calculation via DFPT. In case of a variational approach [30], the total energy in presence of the perturbation is minimized by varying the electronic states. Its explicit expansion is given as

$$\mathscr{E}^{tot} = \mathscr{E}^{tot}[\{\phi_o^{(0)} + \lambda\phi_o^{(1)} + \cdots\}] \tag{10}$$

$$= \mathscr{E}^{(0)} + \lambda\mathscr{E}^{(1)} + \lambda^2\mathscr{E}^{(2)} + \mathscr{O}(\lambda^3) \tag{11}$$

Due to the variational property of the ground state energy, the true ground state orbitals minimize the unperturbed functional. Due to stationarity the linear order energy always vanishes. The first non-vanishing term is thus the second order energy. At the extremal point, this gives the following stationarity condition

$$\frac{\delta\mathscr{E}^{tot}}{\delta\phi_o^{(1)}} = 0 \tag{12}$$

The variation of the electronic states is supplemented by additional constraints in order to maintain the orthonormality of the total states. A particularly convenient choice is the orthogonalization of the $\{\phi^{(1)}\}$ manifold with respect to the $\{\phi^{(0)}\}$ manifold by using the parallel-transport gauge,

$$\langle\phi_o^{(1)}|\phi_{o'}^{(0)}\rangle = 0, \quad \forall o, o'. \tag{13}$$

In this parallel-transport gauge [8, 30], the second order term in the functional expansion of the total energy is given by

$$\mathscr{E}^{(2)} = \sum_o f_o \left[\langle\phi_o^{(1)}|\mathscr{H}_{KS}^{(0)} - \varepsilon_o^{(0)}|\phi_o^{(1)}\rangle\right] + \frac{1}{2}\iint d^3r\, d^3r'\, K(\mathbf{r}, \mathbf{r}')n^{(1)}(\mathbf{r})n^{(1)}(\mathbf{r}')$$

$$+ \sum_o f_o \left[\langle\phi_o^{(1)}|\frac{\delta\mathscr{E}^{pert}}{\delta\langle\phi_o^{(0)}|} + \frac{\delta\mathscr{E}^{pert}}{\delta|\phi_k^{(0)}\rangle}|\phi_o^{(1)}\rangle\right], \tag{14}$$

with the Hartree-exchange-correlation kernel, the KS-Hamiltonian and its eigenvalues given by

$$K(\mathbf{r}, \mathbf{r}') = \frac{\delta(\mathscr{E}_H + \mathscr{E}_{xc})}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \tag{15}$$

$$\mathscr{H}_{KS}^{(0)} = -\frac{1}{2}\nabla^2 + V_{ext} + V_H + V_{xc} \tag{16}$$

$$\varepsilon_o^{(0)} = \langle\phi_o^{(0)}|\mathscr{H}^{KS}|\phi_o^{(0)}\rangle \tag{17}$$

The corresponding Lagrangian for the minimization then is

$$\mathscr{L}^{(2)} = -\mathscr{E}^{(2)} + \sum_{oo'} \langle \phi_o^{(1)} | \phi_{o'}^{(0)} \rangle \Lambda_{o'o}^{(1)}. \tag{18}$$

The Lagrange multipliers $\Lambda_{o'o}^{(1)}$ ensure that the orthogonality according to Eq. (13) is actually imposed during the minimization cycles. Their explicit values can be derived analytically and are related to the mixed expectation values of $\mathscr{H}_{KS}^{(0)}$ between the unperturbed and the perturbed orbitals. For details see the original papers [30].

The resulting Sternheimer equation is an inhomogeneous system of equations

$$-P_e(\mathscr{H}_{KS}^{(0)} - \varepsilon_o^{(0)}) P_e | \phi_o^{(1)} \rangle = P_e \left[ \int d^3 r' K(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}') | \phi_o^{(0)} \rangle + \frac{\delta \mathscr{E}_{KS}^{pert}}{\delta \langle \phi_o^{(0)} |} \right], \tag{19}$$

where $P_e = \sum_o 1 - |\phi_o\rangle\langle\phi_o|$ is a projection operator on the empty orbitals. This equation is usually solved self-consistently by linear algebra algorithms as, e.g., the conjugated-gradient minimization.

With this result it is possible to calculate the response properties for various perturbations such as nuclear displacements or electronic and magnetic fields. In the following it will be applied to the calculation of NMR chemical shifts, which requires the calculation with a perturbation due to an external magnetic field.

## 3 Nuclear Magnetic Resonance

### 3.1 NMR Chemical Shifts from DFPT

Nuclear magnetic resonance spectroscopy (NMR) is a widely used experimental tool to analyze various structural and dynamic properties of molecular, as well as, solid state systems, ranging from simple liquids amorphous and crystalline solids to complex macromolecules of biological relevance [20, 33].

The NMR chemical shifts depend on the local chemical environment of the nuclei and are therefore intrinsically connected to the local electronic structure. Formally, the nuclear spin $\boldsymbol{\mu}_I$ interacts with the external magnetic field via

$$E = -\boldsymbol{\mu}_I \cdot \mathbf{B}^{tot} = -\gamma m \hbar B^{tot}, \tag{20}$$

with the gyromagnetic ratio $\gamma$. This leads to an energy splitting of degenerate spin $m = \pm\frac{1}{2}$ energies of

$$\Delta E = -\gamma \hbar B^{tot}. \tag{21}$$

The total magnetic field is given by

$$\mathbf{B}^{tot}(\mathbf{r}) = \mathbf{B}^{ext} + \mathbf{B}^{ind}(\mathbf{r}), \tag{22}$$

where $\mathbf{B}^{ext}$ is the applied external field and $\mathbf{B}^{ind}(\mathbf{r})$ the induced field modifying the total field acting on the nucleus.

In the linear regime, the induced field $\mathbf{B}^{ind}(\mathbf{r})$ is proportional to the external field; the negative proportionality coefficient is called nuclear shielding:

$$\sigma_{\alpha\beta}(\mathbf{r}) = -\frac{\partial B_{\alpha}^{ind}(\mathbf{r})}{\partial B_{\beta}^{ext}}. \tag{23}$$

The external magnetic field does not directly enter the electronic Hamiltonian. Instead, the underlying vector potential $\mathbf{A}(\mathbf{r})$ is used. They are related via

$$\mathbf{B}^{ext}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r}). \tag{24}$$

The presence of an infinitesimally small external magnetic field $\mathbf{B}^{ext}$ is then included in the electronic Hamiltonian by replacing the kinetic momentum by its canonical equivalent $\mathbf{p} \to \boldsymbol{\pi}$,

$$\boldsymbol{\pi} = \mathbf{p}^{kin} - e\mathbf{A}. \tag{25}$$

This gives rise to the following first-order perturbation Hamiltonian (in atomic units)

$$\mathscr{H}^{(1)} = -\mathbf{p} \cdot \mathbf{A}(\mathbf{r}) = -\mathbf{A}(\mathbf{r}) \cdot \mathbf{p}, \tag{26}$$

since in the Coulomb gauge, the vector potential of a homogeneous magnetic field is then given by

$$\mathbf{A}(\mathbf{r}) = -\frac{1}{2}\mathbf{r} \times \mathbf{B}^{ext}, \tag{27}$$

and thus commutes with $\mathbf{p}$. The choice of the gauge origin should in general not affect the physical observables of a system. This gauge invariance, however, is not trivially guaranteed in numerical computations. The effects of finite basis sets or non-local pseudopotentials introduce origin dependencies which require further corrections. To address these issues, a variety of methods has been developed, as to mention the IGLO [15, 16], GIAO [5] and CSGT [13] gauge.

In periodic systems it is not possible to define the vector potential of a homogeneous magnetic field $\mathbf{B}$. This is due to the ill-definition of the position operator. Also here, various methods have been developed for the calculation of NMR-shifts in extended systems [9, 25, 26, 28, 29, 32, 34].

For finite closed-shell systems, the above definition can be applied and the corresponding first order perturbation functional then is given as

$$\lambda \mathscr{E}^{pert} = \sum_{o} f_o \langle \phi_o | \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) | \phi_o \rangle \tag{28}$$

$$= -\sum_{o} f_o \langle \phi_o | \mathbf{p} \cdot \frac{1}{2}\mathbf{r} \times \mathbf{B}^{ext} | \phi_o \rangle \tag{29}$$

$$= + \sum_o f_o \langle \phi_o | \frac{1}{2} \mathbf{r} \times \mathbf{p} | \phi_o \rangle \cdot \mathbf{B}^{ext}. \tag{30}$$

In the last step, a cyclic permutation of the triple product has been used, which is possible since $p_i r_j$ commute for $i \neq j$.

The remaining dependence of the perturbation on the magnetic field strength is compensated by the $\lambda$ on the left side of the equation, i.e., the magnetic field plays the role of the perturbation parameter. Therefore, effectively three different perturbations for each component are necessary.

The nature of this particular perturbation simplifies the calculation of the perturbed states. Since $\mathbf{r} \times \mathbf{p}$ is Hermitian and purely imaginary in the position representation, the perturbation KS-Hamiltonian and the linear order KS-orbitals are purely imaginary [32].

$$\langle \mathbf{r} | \mathscr{H}^{(1)} | \mathbf{r}' \rangle = \frac{i}{2} \delta(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{R}) \times \mathbf{B} \cdot \nabla \tag{31}$$

Therefore, the linear order density response vanishes analytically

$$n^{(1)}(\mathbf{r}) = \sum_o f_o \left[ \phi_o^{(0)*}(\mathbf{r})\phi_o^{(1)}(\mathbf{r}) + \phi_o^{(1)*}(\mathbf{r})\phi_o^{(0)}(\mathbf{r}) \right] = 0 \quad \forall \mathbf{r}. \tag{32}$$

This is the expected behavior, since magnetic fields should not change the density related physical observables.

In the Sternheimer equation for this perturbation, the dependency on the perturbed density therefore vanishes and no self-consistent solution is required

$$-P_e(\mathscr{H}_{KS}^{(0)} - \varepsilon_o^{(0)}) P_e | \phi_o^{\mathbf{B}} \rangle = P_e \mathbf{r} \times \mathbf{p} | \phi_o^{(0)} \rangle. \tag{33}$$

The $\mathbf{B}$ superscript is a useful shorthand notation for a partial derivative with respect to the $\mathbf{B}$ field and indicates the vector nature of the response

$$| \phi_o^{\mathbf{B}} \rangle = \frac{\partial | \phi_o \rangle}{\partial \mathbf{B}} \tag{34}$$

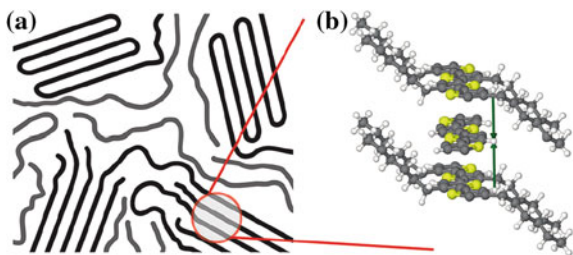$$| \phi_o^{(1)} \rangle = | \phi_o^{\mathbf{B}} \rangle \cdot \mathbf{B} \tag{35}$$

For each of the three perturbation components it is possible to calculate the induced electronic flux

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2} \sum_o f_o \text{Im} \left[ \phi_o^{(1)*} \nabla \phi_o^{(0)} + \phi_o^{(0)*} \nabla \phi_o^{(1)} \right](\mathbf{r}) + n(\mathbf{r})\mathbf{A}(\mathbf{r}) \tag{36}$$

The induced magnetic field then is readily obtained by applying the law of Biot-Savart

$$\mathbf{B}^{ind}(\mathbf{r}) = \int d^3 r' \frac{\mathbf{r}' - \mathbf{r}}{|\mathbf{r}' - \mathbf{r}|^3} \times \mathbf{j}(\mathbf{r}') \tag{37}$$

**Fig. 1** Sketch of the
semicrystalline structure of
(a) and the stacked layers in
the ordered parts (b) P3HT.
Taken from [6]

The shielding tensor then is given by analytically taking the derivative with respect to the external magnetic field $\mathbf{B}^{ext}$.

$$\sigma_{\alpha\beta}(\mathbf{r}) = -\frac{\partial B_{\alpha}^{ind}(\mathbf{r})}{\partial B_{\beta}^{ext}} \tag{38}$$

This final derivative is necessary in order to obtain a result which is independent of the perturbation parameter.

## 3.2 Determination of Supramolecular Packing Motifs from NMR Chemical Shift Calculations

Semicrystalline $\pi$-conjugated polymers such as poly-3-hexyl-thiophene (P3HT) cause broad scientific interest for their application as organic semiconductors. Their local structure is, however, difficult to measure, since they appear in separated phases of high crystallinity as well as amorphous structures, making it impossible to elucidate the exact local structures from e.g. X-ray diffraction. NMR on the other hand gives insight into local phenomena, while the overall structure remains unclear. In a recent study [6] a combined approach of computational as well as experimental spectroscopic investigations led to a successful identification of the local packing.

In that study, X-ray diffraction has been used to determine the unit cell parameters of the system, while intermolecular distance criteria as well as the space group of the system have been extracted from solid-state NMR investigations (cp. Fig. 1). Additionally, the $^1$HNMR chemical shifts have been measured. Based on the possible structures created from the observed distance criteria, calculation of theoretical NMR spectra, or more specifically nuclear independent chemical shieldings (NICS) have been performed. As computationally the NMR chemical shifts are not bound to the nucleus but are calculated from the local electronic properties, in this method the protons (as well as any other elements) chemical shieldings can be computed for any given point in space around the molecules.

**Fig. 2** Different packing models (**a**, **b**, **c**) used to calculate the corresponding NICS maps. Taken from [6]
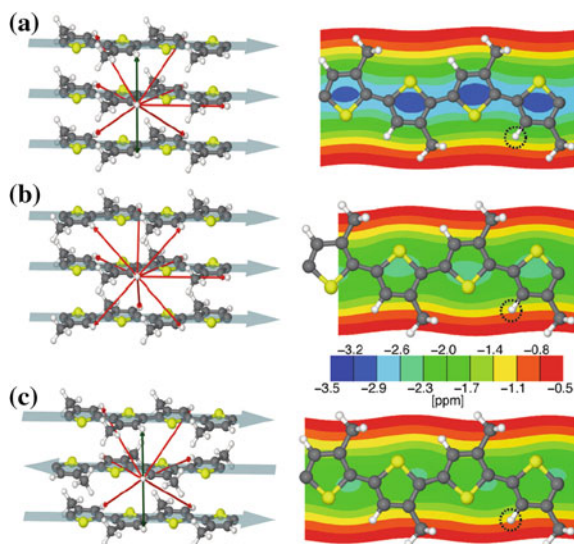
These calculated NICS maps directly show the influence of the packing motives on the local distribution of chemical shifts, displaying an upfield shift by approximately 0.5 ppm for the tiophenes $^{1}$HNMR chemical shift when going from structure (a to structure c) (cp. Fig. 2).

# 4 Van der Waals Interactions

The local-density approximation and gradient corrected approaches to the density functional theory have proven very successful in describing a wide range of systems and their electronic interaction. In case of certain properties related to long range interactions such as the van der Waals interaction, these approximations fail to predict accurate interaction strengths due to the local character of the exchange-correlation functional (see also Chap. "Application of (Kohn–Sham) Density-Functional Theory to Real Materials" by Ghiringhelli).

A lot of effort has been made to overcome this shortcoming, utilizing various approaches [37], ranging from purely empirical corrections, semi-empirical approaches [11], corrections to effective core potentials [3, 21, 35], perturbative approaches [4, 36] up to explicit calculations of the London dispersion forces [1, 17–19, 22, 31].

One of the most widely used approaches, especially due to its inexpensive computation and easy addition to existing implementations is the one proposed by Grimme [10, 11] commonly denoted as DFT-D. In this approach the DFT total energy is corrected by an additive dispersion correction

$$E_{DFT-D} = E_{DFT} + E_{disp} \tag{39}$$

where the dispersion term is given by a Lennard-Jones-type expression according to

$$E_{disp} = -s \sum_i \sum_{j=i+1}^{N} \frac{C_6^{ij}}{r_{ij}} f_{damp}. \tag{40}$$

Here, $f_{damp}$ is a damping function chosen in such a way that the intended interaction behavior is met, but singularities for small $r_{ij}$ are avoided. In this approach, the pairwise coefficients $C_6^{ij}$ are taken as an average of the single contributing atomic $C_6$ coefficients:

$$C_6^{ij} = 2\frac{C_6^i C_6^j}{C_6^i + C_6^j} \tag{41}$$

Usually, these atomic coefficients are determined via an empirical fit to values obtained either from high-level quantum chemical calculations or by comparison with experimental data. An alternative approach is the direct ab-initio calculation within the DFPT framework, which is presented in the following section.

### 4.1 Van der Waals Interactions from DFPT

The most intuitive way of interpreting the van der Waals interaction is the spontaneous polarization of neighboring atoms or molecules due to small instantaneous fluctuations in their electronic densities. These induced dipole moments give rise to the attractive van der Waals interaction. This polarization response can be described by the polarizability mentioned in the introduction of this chapter.

The following derivation follows the approach of Mahan [23, 24]. More recently a computationally inexpensive reformulation has been reported by Nguyen and Gironcoli [27] which uses the Thomas-Fermi von Weizsäcker approximation for the kinetic energy.

Generally, the van der Waals coefficients $C_6^{ij}$ are calculated from the frequency dependent isotropic dipole polarizabilities $\overline{\alpha}_i(iu)$ of the ions $i$ and $j$

$$C_6^{ij} = \frac{3}{\pi} \int \overline{\alpha}_i(iu)\overline{\alpha}_j(iu)du. \tag{42}$$

As already outlined in the introduction of this chapter, the polarizability can be calculated by the second order derivative of the total energy with respect to an applied electric field

$$\alpha_{ab} = \frac{\partial^2 \mathscr{E}_{KS}}{\partial E_a \partial E_b} \tag{43}$$

and hence is accessible via DFPT calculations for an electric field perturbation.

The linearized perturbation functional of an applied external electric field in direction b is

$$\lambda \mathscr{E}^{pert} = -\sum_o f_o \langle \phi_o | \mu_b E_b | \phi_o \rangle. \tag{44}$$

The corresponding generalized Sternheimer equation reads

$$-P_e(\mathscr{H}_{KS}^{(0)} - \varepsilon_o^{(0)}) P_e |\phi_o^{E_b}\rangle = P_e \left[ \int d^3 r' \; K(\mathbf{r}, \mathbf{r}') n^{E_b}(\mathbf{r}') |\phi_o^{(0)}\rangle - 2\mu_b |\phi_o^{(0)}\rangle \right], \tag{45}$$

where $|\phi_o^{E_b}\rangle$ and $n^{E_b}(\mathbf{r}')$ are the linear responses of the orbitals and the electronic density, respectively.

The static polarizability is straightforwardly determined as

$$\alpha_{ab} = 2 \int \mu_a n^{E_b}(\mathbf{r}) d^3 r. \tag{46}$$

For the calculation of the van der Waals coefficients using Eq. (42), the frequency dependent polarizability needs to be determined. Along the lines of Mahan [24], this is achieved by replacing the real eigenvalue $\varepsilon_o^{(0)}$ by a frequency dependent complex one

$$\varepsilon_o^{(0)} \to \varepsilon_o^{(0)} + iu, \tag{47}$$

which yields a complex Sternheimer equation

$$-P_e(\mathscr{H}_{KS}^{(0)} - (\varepsilon_o^{(0)} + iu)) P_e |\tilde{\phi}_o^{E_b}\rangle = P_e \left[ \int d^3 r' K(\mathbf{r}, \mathbf{r}') n^{E_b}(\mathbf{r}') |\phi_o^{(0)}\rangle - 2\mu_b |\phi_o^{(0)}\rangle \right]. \tag{48}$$

This induces an imaginary component in the perturbed orbitals, indicated by the tilde. However, the density response and the Hartree-exchange-correlation kernel remain real due to the cancellation of the linear imaginary contributions in the electronic response density

$$n^{(1)}(\mathbf{r}) = \sum_o f_o [\phi_o^{(0)*}(\mathbf{r}) \tilde{\phi}_o^{(1)}(\mathbf{r}) + \tilde{\phi}_o^{(1)*}(\mathbf{r}) \phi_o^{(0)}(\mathbf{r})]. \tag{49}$$

As for the static polarizability, the frequency dependent polarizability is obtained using Eq. (46). The isotropic polarizability then is given by the trace of the polarizability tensor

$$\bar{\alpha} = \sum_a \alpha_{aa} \tag{50}$$

This approach requires a full self-consistent perturbation calculation for a mesh of imaginary frequencies $(iu)$, which limits its applicability in this form to relatively small systems.
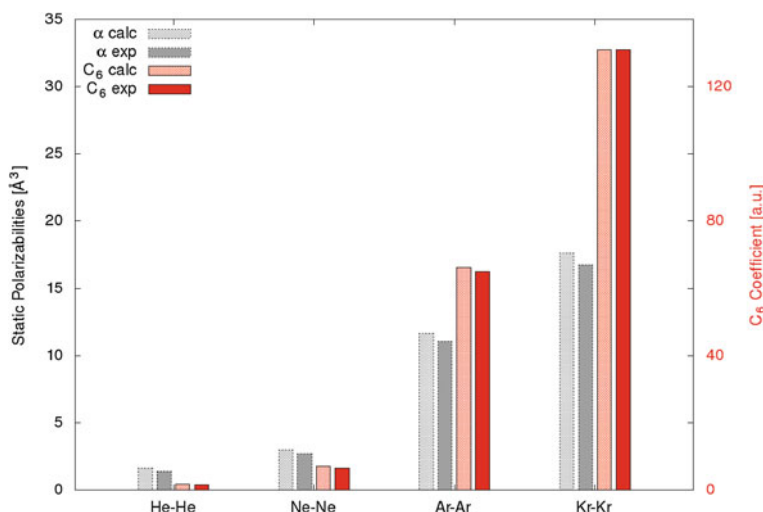
**Fig. 3** Results from the DFPT calculations of van der Waals parameter. Values taken from [24]

A more recent approach by Nguyen and Gironcoli [27] is based on the observation that the polarizability mainly stems from the loosely bound valence electrons in the asymptotic region of the molecules, where typically there are only few dispersed orbitals. This justifies the use of the Thomas-Fermi von Weizsäcker approximation for the kinetic energy, which is considerably simpler and dramatically reduces the necessary computational costs for the calculation of the polarizability at a given frequency (Fig. 3).

## 5 Conclusion

The scope of density functional perturbation theory in the framework of electronic linear response theory covers a wide range of applications. First of all, spectroscopic parameters, which originate from the electronic linear response to an external field perturbation, can be computed from first principles and directly compared to experiment. This covers NMR chemical shifts, as covered in this chapter, but also EPR spectra, infrared and Raman frequencies and intensities, UV/vis absorption lines and X-ray photoelectron spectra. The scope of linear response calculations actually exceeds these spectroscopic parameters, as even van-der-Waals-/dispersion forces can be computed. Hence, density functional perturbation theory provides an important element for the first-principles simulation of real materials and the direct calculation of different spectroscopic and energetic properties.

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