4 Effective Hamiltonians in Chemistry

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1 Introduction

1.1 Why effective Hamiltonians?

Effective Hamiltonians (EHs) occupy an important place in quantum chemistry. EHs serve a multitude of different purposes. On the one hand, they are vital in the formulation of new approximate methods that lead to new computationally efficient tools. On the other hand, they allow one to recast highly complex problems that are difficult to understand into seemingly simpler problems that are amenable to human analysis. In this latter application, they unfold their full power by creating models that can be used to highlight the physical essence of the problem at hand. In many cases, the emerging model Hamiltonians are of low dimension and can be solved by hand or with very little computational effort. The crucial step is that the matrix elements of the EH can be recast in terms of effective parameters. The latter are adjustable and can, for example, be fitted to experiments or higher-level calculations. The benefit of EH theory is here that: a) the model Hamiltonians are derived from more complete Hamiltonians; hence the theory provides explicit and concrete expressions that allow the calculation of the model parameters and b) being derived from first principles, these model Hamiltonians are solidly grounded in fundamental physics. Thus, the effective Hamiltonians derived in this way do not just represent a curve fitting exercise of uncertain physical content and interpretation as would be the case for model Hamiltonians that are only based on physical intuition or conjecture.

The effective Hamiltonian concept can even be taken a step further and effective Hamiltonians can be derived from more elaborate effective Hamiltonians that themselves are derived from first-principles physics. The important point is that there is an unbroken chain of logic that leads by pure deduction from first physical principles to a simple, intuitively appealing, and physically sound model that can be used to interpret the results of measurements or even the behavior of entire classes of substances or materials. The benefit of having model Hamiltonians derived in this way can hardly be overemphasized since the theory does not only provide a concrete and unambiguous way to compute the model parameters, but it also makes it clear under which conditions the model Hamiltonian is valid and when it is expected to break down. A concrete example for such a situation that will be discussed in more detail in section 3.2 is the spin Hamiltonian (SH) used to interpret magnetic measurements (electron paramagnetic resonance, EPR or nuclear magnetic resonance, NMR) on molecules or solids. The SH is derived conveniently from the time-independent relativistic many-particle Schrödinger equation (technically the Dirac-Coulomb-Breit (DCB) Hamiltonian). It leads to a low-dimensional model Hamiltonian that contains the SH parameters as adjustable parameters. These are the g-matrix, the hyperfine coupling (HFC) matrix, the zero-field splitting (ZFS, in physics often referred to as the magnetic anisotropy), the quadrupole splitting, the chemical shift and the nuclear spin-spin coupling. For interacting magnetic systems, the familiar Heisenberg exchange Hamiltonian is obtained from the theory.

However, once there are enough spins in a given system (for example in clusters containing a dozen to a few dozen open-shell transition metal ions), even the SH dimensions become

unmanageable and can reach dimensions of hundreds of millions. Quite frequently, one is only interested in the lowest few eigenstates of such a system that are thermally accessible over a given temperature range. In this case, one wants to describe these few magnetic sublevels with an effective Hamiltonian that can be derived from the enormous SH of the entire system. The parameters that enter this secondary SH are then functions of all the spins and SH parameters of the full system. A very simple concrete example would be an $S = 5/2$ system with strong ZFS (relative to external magnetic fields). Such a system contains $2S+1 = 6$ magnetic sublevels that, by means of Kramers degeneracy, form three so-called "Kramers doublets". The latter can each be described by an effective Hamiltonian with spin $S = 1/2$. Hence, three pseudo $S = 1/2$ systems substitute for the entire $S = 5/2$ system. We refer to the specialist literature for further details [1, 2].

In this chapter, we will provide an introduction into the theory of effective Hamiltonians. We will cover formal aspects in section 2 before proceeding to actual chemical applications in section 3 that will discuss both computational tools for the calculation of static ("strong" in physics language) and dynamic electron correlation as well as EHs derived to parameterize and understand magnetic properties. An example for the combination of both strategies will conclude our chapter.

1.2 An introduction into quantum-chemical notation

Since we will present the material covered in this chapter mostly from a quantum chemistry point of view, it is convenient to briefly discuss the point of departure of the theory and introduce the necessary notation along the way.

1.2.1 One-particle and many-particle Hamiltonians

We start from the nonrelativistic many-particle Hamiltonian in the Born-Oppenheimer (BO) approximation (clamped nuclei), which is simply given by

$$\hat{H}_{\text{BO}} = \sum_i \hat{h}(\mathbf{x}_i) + \tfrac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \tfrac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \qquad (1)$$

with the one-electron part of the Hamiltonian given by the sum of the kinetic energy and nucleus-electron attraction terms,

$$\hat{h}(\mathbf{x}_i) = -\tfrac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}. \qquad (2)$$

Here, we consider a system consisting of N electrons and M nuclei. The electrons are described by the coordinates $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$, where $\mathbf{r}_i$ is the set of three position variables for the i'th electron and σ_i represents its spin degree of freedom (spin-up, α, $\uparrow$ or spin-down, β, $\downarrow$). The nuclei are assumed to be at rest at positions $\mathbf{R}_A$ and have nuclear charges Z_A (for the A'th nucleus). Hartree atomic units ($4\pi\varepsilon_0 = \hbar = e = m_e = 1$) [3] are used throughout.

In this chapter, we will remain within the confines of the time-independent Schrödinger equation

$$\hat{H}_{\text{BO}}\Psi_I(\mathbf{x}|\mathbf{R}) = E_I(\mathbf{R})\Psi_I(\mathbf{x}|\mathbf{R}), \tag{3}$$

where $\mathbf{x}$ and $\mathbf{R}$ denote the collection of all electronic and nuclear degrees of freedom respectively and the notation $\Psi(\mathbf{x}|\mathbf{R})$ indicates that the many particle wavefunction depends explicitly on the electron coordinates and parametrically on the nuclear coordinates. In order to be concise, we will follow the convention of using uppercase letters and indices for many-electron quantities and lowercase letters, symbols, and indices for one-electron quantities. Thus, $I = 0, ..., \infty$ enumerates the possible electronic eigenstates of the BO Hamiltonian.

While conceptually simple, the BO Schrödinger equation cannot be solved analytically even for a two-electron system such as the helium atom. However, very powerful approximations have been developed over the course of the last century. Many of them begin with a model of effective independent particles (Hartree-Fock method, HF). In the HF method one replaces the many-particle equation by an effective one-particle equation of the form

$$\hat{F}(\{\psi\})\psi_i(\mathbf{x}) = \varepsilon_i\psi_i(\mathbf{x}). \tag{4}$$

The HF equations are readily derived from the BO Schrödinger equation and the variational principle [3]. The effective one-particle operator $\hat{F}$ depends on its own solutions (the set of one-particle functions $\{\psi\}$) and yields the orbital energies ε_i and orbitals $\psi_i(\mathbf{x})$. Given the dependence of $\hat{F}$ on its own solutions, the HF equations must be solved by iteration starting from a set of trial orbitals. We will write down an explicit form of the Fock operator after introducing second-quantized notation (see Eq. (13) below).

In general, the HF equations do not only have N solutions, but an infinite number of solutions. The lowest N orbitals are referred to as "occupied orbitals" of the system and they are usually denoted with the indices i, j, k, l. The remaining orbitals are the leftover solutions of the variational principle and are referred to as unoccupied or "virtual" orbitals with indices customarily denoted by a, b, c, d. This corresponds to the particle-hole convention frequently encountered in physics. General orbitals are given the indices p, q, r, s.

The set of occupied orbitals $\{\psi\}$ are the building blocks of the HF wavefunction, which is an antisymmetrized product ("Slater determinant")

$$\Psi_{\text{HF}}(\mathbf{x}_1 \dots \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix} \equiv |\psi_1...\psi_N|. \tag{5}$$

Occasionally, an overbar is used in order to indicate occupation of an orbital with a spin down electron, while no overbar indicates a spin-up electron, e.g. $|\psi_1\bar{\psi}_1...\bar{\psi}_i...\psi_j...\psi_N|$. The HF wavefunction is a mean-field approximation to the mind-boggling complexity of the exact ground state many-particle wavefunction.

It is our experience that much confusion arises from not properly differentiating between the many-particle and single-particle levels. Hence, in this chapter, we will make a dedicated effort

to be clear at which level we are arguing. We note in passing that only the eigenspectrum of the many-particle Hamiltonian (and the associated properties of the many-particle wavefunctions) are directly related to observable quantities. The orbitals and orbital energies are not observables and they are not related to observable quantities. For the purpose of the theory, they are simply auxiliary quantities used to construct better and better approximations to the many-particle wavefunction(s) of the system. In chemistry, the term "state" is reserved for the many-particle eigenfunctions of the Schrödinger equation (or approximations thereof). Orbitals are not referred to as "states". Hence, in chemical language, there also can be no notion of "occupied states" or "unoccupied states".

1.2.2   Electron correlation and the correlation energy

While the HF method yields a fairly good approximation to the total energy of the system (about 99.8% correct), the remaining 0.2% error are very large on the chemical energy scale. For a somewhat larger system the error can easily reach 10 E_h which translates to more than 270 eV. Hence, in absolute terms, the error of the HF approximation is very large and one needs to proceed beyond the HF approximation. By definition, the difference between the exact energy and the HF energy is referred to as the "correlation energy"

$$E_\mathrm{corr} = E_\mathrm{exact} - E_\mathrm{HF}. \tag{6}$$

By definition, the correlation energy is always negative. If the system is conceptionally well-described by a single Slater determinant, then all of the correlation energy is referred to as "dynamic" correlation energy. The physical picture being that the instantaneous electron-electron interaction provides a correction to the mean-field HF method. If, however, the system is not well described by a single Slater determinant, the energy gained by choosing a qualitatively correct "ansatz" is referred to as "static" correlation energy. An example would be the H_2 molecule towards its dissociation limit that requires two Slater determinants for a qualitatively correct description. From this description, it is already evident that the distinction between static and dynamic correlation is vague, ill-defined, and not unique. We will not dwell on the subject here. The shortcomings of the HF model are conceptually readily remedied. To this end, we will make use of second-quantization notation and introduce the electron replacement operators

$$a_p^q = a_q^\dagger a_p, \tag{7}$$

where $a_q^\dagger$ and a_p are the familiar fermion creation and annihilation operators, respectively. Since most of the presented theory as well as the BO Hamiltonian do not explicitly contain spin operators, it is convenient to define the spin-traced excitation operators (also called "generators of the unitary group")

$$E_p^q = a_{\bar{p}}^{\bar{q}} + a_p^q. \tag{8}$$

The operator E_p^q is a singlet excitation operator, i.e., it does not change the total spin of the state on which it acts.

Obviously, these operators refer to a specific one-particle basis. This is usually taken to be the set of HF orbitals. The HF orbitals themselves can not, however, be exactly calculated in practice. In quantum chemistry, it is common to expand them into a fixed, finite set of atom-centered basis functions $\{\varphi\}$ as

$$\psi_i(\mathbf{x}) = \sum_\mu c_{\mu i} \varphi_\mu(\mathbf{x}). \tag{9}$$

The actual functional form of the basis function is usually taken to be of the Gaussian type but details would lead too far astray here.

In terms of the second-quantized operators, the BO Hamiltonian reads

$$\hat{H}_{\mathrm{BO}} = \sum_{p,q} h_{pq} E_q^p + \tfrac{1}{2} \sum_{p,q,r,s} g_{pr}^{qs}(E_q^p E_s^r - E_s^p \delta_{qr}). \tag{10}$$

Since the BO Hamiltonian can be written entirely in terms of singlet excitation operators, it is clear that it conserves the total spin S. In Eq. (10), the nuclear repulsion term has been dropped for convenience. Furthermore, the one- and two-electron integrals have been introduced:

$$h_{pq} = \left\langle \psi_p | \hat{h} | \psi_q \right\rangle, \tag{11}$$

$$g_{pr}^{qs} = \left(\psi_p \psi_q | \psi_r \psi_s\right) \equiv \left\langle \psi_p \psi_r | \psi_q \psi_s \right\rangle. \tag{12}$$

In chemistry the round bracket notation $(11|22)$ is more common, while in physics the bracket notation $\langle 12|12 \rangle$ is usually preferred ('1' and '2' refer to the coordinates of electrons 1 and 2, respectively). The second-quantized BO operator is only equivalent to its first-quantized counterpart in the limit that the one-particle basis is mathematically complete. This is never the case in practice and consequently, the second-quantized BO Hamiltonian can be regarded as the projection of the BO Schrödinger equation onto the finite one-particle basis.

With the definition of the one- and two-electron integrals, we can give an explicit form of the Fock operator. It is represented by the matrix

$$F_{pq} = h_{pq} + \sum_k \underbrace{\left[\left\langle \psi_p \psi_k | \psi_q \psi_k \right\rangle - \left\langle \psi_p \psi_k | \psi_k \psi_q \right\rangle\right]}_{\equiv \langle pk||qk \rangle}, \tag{13}$$

where the antisymmetrized two-electron repulsion integral $\langle pk||qk \rangle$ has been introduced. The negative term in the sum over k is the "exchange" term. It arises from the electrostatic repulsion of the electrons among each other in conjunction with the antisymmetry requirements of the fermionic many-particle wavefunction. It does not represent an "exchange force".

Given the second-quantized notation, it is straightforward to write down an expansion of the many-particle ground-state wavefunction:

$$|\Psi_0\rangle = |\Psi_{\mathrm{HF}}\rangle + \sum_{i,a} C_i^a |\Phi_i^a\rangle + \left(\tfrac{1}{2!}\right)^2 \sum_{i,j,a,b} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \left(\tfrac{1}{3!}\right)^2 \sum_{i,j,k,a,b,c} C_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + ... \tag{14}$$

Here, the building blocks $|\Phi_{i...}^{a...}\rangle$ are determinants in which one-, two-, three- ... up to N orbitals have been replaced in the HF determinant, e.g.

$$|\Phi_i^a\rangle = a_i^a |\Psi_{\mathrm{HF}}\rangle \tag{15}$$

etc. In the language of second quantization, the HF determinant acts as the "Fermi vacuum". The coefficients C_i^a ... are wavefunction parameters that must be determined in one way or another. If this is done variationally, one refers to the method as "configuration interaction" (CI). If perturbation theory is used, "many body perturbation theory" (MBPT) arises. If CI is done with all possible Slater determinants, the method of Full CI (FCI) arises. It represents the exact solution of the Schrödinger equation in the chosen finite basis. Since the number of possible Slater determinants grows factorially, this method is restricted to very small systems. However, it serves as an invaluable benchmark for approximate methods.

Truncated CI expansion have the very undesirable property of not being size-consistent, i.e., the energy of two non-interacting systems is not the sum of the energy of the individual systems calculated in the same approximation. Hence, truncated CI has essentially been abandoned. The method of coupled-cluster (CC) theory does not suffer from this shortcoming. Here, one uses an exponential ansatz

$$|\Psi_0\rangle = \exp(\hat{T})\,|\Psi_{\text{HF}}\rangle \tag{16}$$

with the cluster operator being the sum of one-, two-, ... particle excitation operators,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + ... = \sum_{i,a} t_i^a a_i^a + \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab} a_j^b a_i^a + ... \tag{17}$$

CC theory is nonlinear and therefore more complex than CI. However, it is size-consistent and extensive at any truncation level of the cluster operator and consequently the method of choice. Truncated MBPT is also size-consistent and frequently used in chemistry.

1.2.3   Relativistic and external field terms

In order to relate to the material presented in section 3, we need to briefly mention extensions to the BO Hamiltonian. Next to many other terms, these corrections arise either from relativity or the presence of external electric or magnetic fields.

All relativistic terms can be derived from the DCB Hamiltonian and are usually grouped into spin-free ("scalar") and spin-dependent terms. Among the numerous terms that arise, the most important relativistic term for our discussion is the spin-orbit coupling (SOC). The SOC is in general a complex two-electron operator. Here, we represent it in a spin-orbit mean-field (SOMF) approximation [4,5] that can be written in the form

$$\hat{H}_{\text{SOC}} \approx \sum_i \mathbf{h}_i^{\text{SOC}} \hat{\mathbf{s}}_i. \tag{18}$$

Here, $\hat{\mathbf{s}}_i$ is the spin of the i'th electron and $\mathbf{h}^{\text{SOC}}$ is an effective SOC operator with purely imaginary matrix elements.

Since the BO Hamiltonian is spin-free, it commutes with the total spin $\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i$ and consequently, the eigenfunctions of the BO Hamiltonian can be labeled according to two additional quantum numbers S (the total spin) and $M = S, S-1, ..., -S$ (the projection of the total spin onto the z axis). At the level of the BO Hamiltonian all M-components ("magnetic sublevels")

of a given S and electronic state I are exactly degenerate (they form a "spin multiplet"). This degeneracy is lifted by the SOC which mixes states of different S and M. It is essential to properly differentiate between the total spin $\hat{\mathbf{S}}$ and the individual spins $\hat{\mathbf{s}}_i$ when discussing magnetic properties.

Other contributions to the Hamiltonian will be briefly visited in section 3.2.

2 Theory of effective Hamiltonians

2.1 Effective Hamiltonians via similarity transformation

Let H be the "complete" Hamiltonian describing a quantum system, e.g. the BO or DCB Hamiltonians introduced above. Its eigenvalues and eigenstates fulfill the time-independent Schrödinger equation

$$H|\Psi_I\rangle = E_I|\Psi_I\rangle. \tag{19}$$

As already mentioned in the introduction, it can be inconvenient to work with this Hamiltonian if it has a large number of eigenstates and eigenvalues, since usually one is only interested in the low-energy part of the spectrum. One can then define an "exact" effective Hamiltonian that acts in a subspace of reduced dimensionality and reproduces the exact eigenvalues for a limited number of eigenstates of H,

$$H^{\text{eff}}|\tilde{\Psi}_I\rangle = E_I|\tilde{\Psi}_I\rangle. \tag{20}$$

The eigenstates $|\tilde{\Psi}_I\rangle$ need not be identical to the true eigenstates $|\Psi_I\rangle$. However, they are usually required to provide a qualitatively correct physical description of the true eigenstates.

One can formulate effective Hamiltonian theory very generally on the basis of similarity transformations. This was done by Shavitt and Redmon [6] and we follow their treatment in the following. The theory was also summarized in a recent dissertation [7]. Let $\mathcal{H}$ be the complete Hilbert space on which H acts. A given basis of this Hilbert space is then divided into two orthogonal subsets: The "model space" $\mathcal{H}_0$ with projector $P = \sum_{I\in\text{model}} |\Phi_I\rangle\langle\Phi_I|$ and the complementary or outer space $\mathcal{H}_{\text{outer}}$ with projector $Q = 1-P = \sum_{K\in\text{outer}} |\Phi_K\rangle\langle\Phi_K|$. In the following, we use indices $I, J, ...$ to refer to states in the model space and indices $K, L, ...$ to refer to states in the outer space. The model space will be the space on which the effective Hamiltonian acts. Once the model space is chosen, an arbitrary operator A can be decomposed as [6]

$$A = A_D + A_X, \tag{21}$$

where

$$A_D = PAP + QAQ \tag{22}$$

is called its block diagonal part and

$$A_X = PAQ + QAP \tag{23}$$

is called its block off-diagonal part. The essence of effective Hamiltonian theory can now be described as finding a so-called decoupling operator U such that the similarity-transformed

Hamiltonian

$$\tilde{H} = U^{-1}HU \tag{24}$$

is block-diagonal [6]. The effective Hamiltonian is then defined as the model-space part of the similarity-transformed Hamiltonian, i.e.

$$H^{\text{eff}} = P\tilde{H}P. \tag{25}$$

If one assumes that the energies E_I and model-space states $|\tilde{\Psi}_I\rangle$ fulfill the eigenvalue equation (20), it is easy to show that

$$HU|\tilde{\Psi}_I\rangle = U\tilde{H}|\tilde{\Psi}_I\rangle = E_I U|\tilde{\Psi}_I\rangle. \tag{26}$$

This shows that $|\Psi_I\rangle = U|\tilde{\Psi}_I\rangle$ are exact eigenfunctions and the E_I the corresponding exact eigenenergies of the full Hamiltonian H. The requirements formulated so far still leave many different possible choices for the decoupling operator U.

2.2   Choice of the decoupling operator: Bloch and van Vleck

We already mentioned that the eigenstates of the effective Hamiltonian are usually required to give a qualitatively correct description of the true eigenstates.

One common choice that fulfills this requirement consists in setting $U_D = 1$ [6], where U_D is defined as the block diagonal part (see Eq. (22)) of the decoupling operator U. This leads to

$$|\tilde{\Psi}_I\rangle = P|\Psi_I\rangle, \tag{27}$$

i.e., the eigenstates of the effective Hamiltonian are orthogonal projections of the exact eigenstates on the model space. For this choice, the effective Hamiltonian, which is named after Bloch [8], can be written

$$H^{\text{eff}} = PH\Omega, \tag{28}$$

where the so-called wave operator Ω is defined as

$$\Omega = UP. \tag{29}$$

The wave operator is a solution of the equation

$$\Omega H \Omega = H\Omega, \tag{30}$$

which is a nonperturbative version [9] of the so-called generalized Bloch equation [10]. Since its eigenstates are – as projections on the model space – in general not orthogonal, the Bloch effective Hamiltonian is in general not Hermitian.

Another choice for U is given by the canonical Van Vleck approach [6], where the decoupling operator is defined as

$$U = \exp(G) \tag{31}$$

with G being an anti-Hermitian ($G^\dagger = -G$) and block off-diagonal ($G_D = 0$) operator. Since G is anti-Hermitian, U is unitary with this choice ($U^\dagger U = 1$). Hence, the eigenstates of the effective Hamiltonian are orthogonal,

$$\langle \tilde{\Psi}_I | \tilde{\Psi}_J \rangle = \langle \tilde{\Psi}_I | U^\dagger U | \tilde{\Psi}_J \rangle = \langle \Psi_I | \Psi_J \rangle = \delta_{IJ}. \tag{32}$$

This also means that the effective Hamiltonian in the canonical Van Vleck approach is Hermitian. One can show that the eigenstates of the Bloch (label B) and the canonical van Vleck (label C) effective Hamiltonians are related by symmetric orthonormalization [6],

$$|\tilde{\Psi}_I^C\rangle = \sum_J |\tilde{\Psi}_J^B\rangle S_{JI}^{-1/2}. \tag{33}$$

Here, $S_{JI} = \langle \tilde{\Psi}_J^B | \tilde{\Psi}_I^B \rangle$ is the positive-definite overlap matrix of the Bloch eigenstates. It should be mentioned that the canonical van Vleck effective Hamiltonian turns out to be identical to the effective Hamiltonian introduced by des Cloizeaux [11], as discussed by Klein [12] and Brandow [13, 14].

If the eigenstates and eigenvalues of the effective Hamiltonians are known, it is possible to write them via a spectral decomposition. The Bloch effective Hamiltonian can be written as

$$H_B^{\text{eff}} = \sum_I |\tilde{\Psi}_I^B\rangle E_I \langle \tilde{\Psi}_I^D |, \tag{34}$$

where

$$|\tilde{\Psi}_I^D\rangle = \sum_J |\tilde{\Psi}_J^B\rangle S_{JI}^{-1} \tag{35}$$

defines the state that is dual (also called contravariant) to the state $|\tilde{\Psi}_I^B\rangle$. The dual states are the unique set of states that are biorthogonal to the original set of Bloch eigenstates,

$$\langle \tilde{\Psi}_I^D | \tilde{\Psi}_J^B \rangle = \delta_{IJ}. \tag{36}$$

The canonical van Vleck / des Cloizeaux effective Hamiltonian can be written as

$$H_C^{\text{eff}} = \sum_I |\tilde{\Psi}_I^C\rangle E_I \langle \tilde{\Psi}_I^C |. \tag{37}$$

The quality of the chosen model space can be quantitatively defined by the norm of the projected states $|\tilde{\Psi}_I^B\rangle$, which is given by the diagonal of the overlap matrix S_{II}. The closer these norms are to 1, the less severe is the non-Hermiticity of the Bloch effective Hamiltonian and the smaller is the difference between the Bloch and canonical van Vleck effective Hamiltonian.

2.3 Partitioning method

Another approach to the construction of effective Hamiltonians, called the partitioning method, was introduced by Löwdin [15–17]. It starts by dividing the Hilbert space into a model space

A (corresponding to $\mathcal{H}_0$ from above) and a remainder B (corresponding to $\mathcal{H}_{\text{outer}}$ from above). The time-independent Schrödinger equation can then be written in block matrix form as

$$\begin{pmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{BA} & \mathbf{H}_{BB} \end{pmatrix} \begin{pmatrix} \mathbf{C}_A \\ \mathbf{C}_B \end{pmatrix} = E \begin{pmatrix} \mathbf{C}_A \\ \mathbf{C}_B \end{pmatrix}. \tag{38}$$

This can be rewritten in terms of two coupled equations

$$\mathbf{H}_{AA}\mathbf{C}_A + \mathbf{H}_{AB}\mathbf{C}_B = E\mathbf{C}_A, \tag{39}$$

$$\mathbf{H}_{BA}\mathbf{C}_A + \mathbf{H}_{BB}\mathbf{C}_B = E\mathbf{C}_B. \tag{40}$$

From Eq. (40) one can obtain

$$\mathbf{C}_B = (E - \mathbf{H}_{BB})^{-1}\mathbf{H}_{BA}\mathbf{C}_A, \tag{41}$$

which can be inserted into Eq. (39) to eliminate $\mathbf{C}_B$ and obtain

$$\mathbf{H}_{AA}^{\text{eff}}(E)\mathbf{C}_A = E\mathbf{C}_A. \tag{42}$$

The energy-dependent A-space effective Hamiltonian is given by

$$\mathbf{H}_{AA}^{\text{eff}}(E) = \mathbf{H}_{AA} + \mathbf{H}_{AB}(E - \mathbf{H}_{BB})^{-1}\mathbf{H}_{BA}. \tag{43}$$

One can see that the effective Hamiltonian consists of the A block of the original Hamiltonian "dressed" with the matrix $\mathbf{H}_{AB}(E - \mathbf{H}_{BB})^{-1}\mathbf{H}_{BA}$. The inverse $(E - \mathbf{H}_{BB})^{-1}$ exists if E does not overlap with the spectrum of $\mathbf{H}_{BB}$. Diagonalization of the effective Hamiltonian Eq. (43) gives $\mathbf{C}_A$, the projection of the exact eigenstate with energy E on the model space. A drawback is that the effective Hamiltonian is a function of the exact energy E, which is unknown unless one solves the full problem first.

2.4 Intermediate effective Hamiltonians

In section 2.2 we made the assumption that there is a one-to-one mapping between eigenstates $|\tilde{\Psi}_I\rangle$ of the effective Hamiltonian in the model space and the same number of exact eigenstates $|\Psi_I\rangle$. Sometimes this identification is ambiguous or not even possible. For example, the qualitatively correct description of the electronic ground state of the Be atom requires two electron configurations. Apart from the dominant $(1s)^2(2s)^2$ configuration, also $(1s)^2(2p)^2$ is needed [18]. This means that at least these two configurations should be included in the model space. However, it is not possible to identify a bound excited state of the Be atom that has $(1s)^2(2p)^2$ as its dominant configuration [19]. In such a case, the effective Hamiltonian is not well-defined and its perturbative expansion (see the next section) will often diverge.

To solve this problem, Malrieu and coworkers have introduced the concept of intermediate effective Hamiltonians (IEH) [20]. One defines an IEH H^{int} by the requirement that the equation

$$H^{\text{int}}P|\Psi_I\rangle = E_I P|\Psi_I\rangle \tag{44}$$

from Bloch effective Hamiltonian theory is only fulfilled for a number N_m of exact eigenstates $|\Psi_I\rangle$ that is *smaller* than the dimension of the model space. The whole model space is divided into the "main model space" containing N_m determinants that dominate the states of interest and the "intermediate space" containing all remaining determinants. They explicitly contribute to the solutions of interest and act as a "buffer space" between the main model space and the outer space. Eq. (44) apparently does not define the IEH uniquely; hence there is a large variety of different intermediate Hamiltonians.

If the IEH gives only a single exact energy and projection of an exact eigenstate, it is called a state-specific intermediate Hamiltonian. An example of this is the partitioning technique effective Hamiltonian (Eq. (43)) introduced in the last section [19].

2.5 Perturbative expansion of effective Hamiltonians

The definitions of the effective Hamiltonians given in the previous sections all require that the solution of the full problem is known first, i.e., they do not provide a computational simplification. Perturbation theory provides a means to construct these effective Hamiltonians without prior knowledge of the exact solutions. Here, the Hamiltonian is separated into a zeroth-order Hamiltonian and a perturbation,

$$H = H_0 + V. \tag{45}$$

The eigenvalues and eigenstates of the zeroth-order Hamiltonian must be known,

$$H_0|\Psi_I^{(0)}\rangle = E_I^{(0)}|\Psi_I^{(0)}\rangle, \tag{46}$$

and V is supposed to be small compared to H_0.

The derivation of the final equations would go beyond the scope of the present chapter. Therefore, we just present the results together with the relevant literature references. We also restrict ourselves to expansions up to second order, which are most relevant in practice.

2.5.1 Quasidegenerate perturbation theory

The expansion of the Bloch effective Hamiltonian in orders of the perturbation operator V (also known as quasidegenerate perturbation theory, QDPT) gives up to second order [6]

$$\langle\Psi_I^{(0)}|H_{\mathrm{B}}^{\mathrm{eff}(0-2)}|\Psi_J^{(0)}\rangle = H_{IJ} + \sum_K \frac{\langle\Psi_I^{(0)}|H|\Psi_K^{(0)}\rangle\langle\Psi_K^{(0)}|H|\Psi_J^{(0)}\rangle}{E_J^{(0)} - E_K^{(0)}}. \tag{47}$$

This effective Hamiltonian is the "bare" Hamiltonian within the model space plus a "dressing", a form that was already observed for the partitioning technique effective Hamiltonian above. From the presence of the index J in the denominator, it becomes apparent that the effective Hamiltonian is not Hermitian. Up to second order (but not at higher orders), it turns out that the canonical Van Vleck / des Cloizeaux effective Hamiltonian is simply the Hermitization of the corresponding Bloch second-order effective Hamiltonian [6],

$$\mathbf{H}_{\mathrm{C}}^{\mathrm{eff}(0-2)} = \frac{1}{2}\Big(\mathbf{H}_{\mathrm{B}}^{\mathrm{eff}(0-2)} + \mathbf{H}_{\mathrm{B}}^{\mathrm{eff}(0-2)\dagger}\Big). \tag{48}$$

If all states in the model space have the same 0th order energy $E_I^{(0)} = E^{(0)}$, the 2nd order Bloch and canonical van Vleck effective Hamiltonians are identical and given by

$$H_{IJ}^{\text{eff}(0-2)} = H_{IJ} + \sum_K \frac{\langle \Psi_I^{(0)} | H | \Psi_K^{(0)} \rangle \langle \Psi_K^{(0)} | H | \Psi_J^{(0)} \rangle}{E^{(0)} - E_K^{(0)}}. \tag{49}$$

This is the common degenerate perturbation theory (DPT) expression up to second order. For a one-dimensional model space (where the effective Hamiltonian is equal to the energy), this reduces to the well-known nondegenerate Rayleigh-Schrödinger perturbation theory formula.

2.5.2 Expansion of the partitioning technique effective Hamiltonian

One can show that [17]

$$\begin{aligned}
\left(E - \mathbf{H}_{BB}\right)^{-1} &= \left(E - \mathbf{H}_{BB}^{(0)}\right)^{-1} + \left(E - \mathbf{H}_{BB}^{(0)}\right)^{-1} \mathbf{V}_{BB} \left(E - \mathbf{H}_{BB}^{(0)}\right)^{-1} \\
&\quad + \left(E - \mathbf{H}_{BB}^{(0)}\right)^{-1} \mathbf{V}_{BB} \left(E - \mathbf{H}_{BB}^{(0)}\right)^{-1} \mathbf{V}_{BB} \left(E - \mathbf{H}_{BB}^{(0)}\right)^{-1} + \dots
\end{aligned} \tag{50}$$

If this is inserted into Eq. (43), one obtains the well-known Brillouin-Wigner (BW) perturbation series. Truncated at the 2nd order, the BW effective Hamiltonian is

$$\mathbf{H}_{AA}^{\text{eff}}(E) \approx \mathbf{H}_{AA} + \mathbf{H}_{AB} \left(E - \mathbf{H}_{BB}^{(0)}\right)^{-1} \mathbf{H}_{BA}. \tag{51}$$

In a basis of eigenstates $|\Psi_I^{(0)}\rangle \in A$ and $|\Psi_K^{(0)}\rangle \in B$ of the 0th order Hamiltonian, one can use $\langle \Psi_K^{(0)} | H_{BB}^{(0)} | \Psi_L^{(0)} \rangle = E_K^{(0)} \delta_{KL}$ to write the effective Hamiltonian as

$$H_{IJ}^{\text{eff}}(E) \approx H_{IJ} + \sum_{K \in B} \frac{\langle \Psi_I^{(0)} | H | \Psi_K^{(0)} \rangle \langle \Psi_K^{(0)} | H | \Psi_J^{(0)} \rangle}{E - E_K^{(0)}}. \tag{52}$$

If a good approximation $E^{(0)}$ to the exact energy E is known, this can be simplified to an energy-independent effective Hamiltonian

$$H_{IJ}^{\text{eff}} \approx H_{IJ} + \sum_{K \in B} \frac{\langle \Psi_I^{(0)} | H | \Psi_K^{(0)} \rangle \langle \Psi_K^{(0)} | H | \Psi_J^{(0)} \rangle}{E^{(0)} - E_K^{(0)}} \tag{53}$$

that is equivalent to the so-called "shifted B_k" [21] method. If there is a one-to-one map between the states spanning the model space A and the same number of exact eigenstates of the Hamiltonian, then the same model space can be used for all of them, but the state-specific effective Hamiltonians Eq. (53) are in general different for each of those states. However, in the special case that the same $E^{(0)}$ is a reasonable zeroth-order energy for all the states in the model space, Eq. (53) can be considered as an effective Hamiltonian delivering all energies and projections on the model space simultaneously. One can see that this is identical to the DPT expression discussed in the previous section.

2.5.3　Generalized degenerate perturbation theory

We finally mention the perturbative expansion of the first state-specific intermediate Hamiltonian introduced by Malrieu *et al.* in their seminal paper [20]. It is called generalized degenerate perturbation theory (GDPT). Up to second order, the intermediate Hamiltonian is given by

$$H_{IJ}^{\text{int}(0-2)} = H_{IJ} + \sum_K \frac{\langle \Psi_I^{(0)} | H | \Psi_K^{(0)} \rangle \langle \Psi_K^{(0)} | H | \Psi_J^{(0)} \rangle}{E^{(0)} - E_K^{(0)}}. \tag{54}$$

This is equivalent to the shifted-B_k effective Hamiltonian (see Eq. (53)) as was already recognized by Malrieu and coworkers [20]. This expression also forms the basis for the recently introduced dynamic correlation dressed complete active space method (DCD-CAS(2)) [22, 23]. The results of this section show that often one can end up with similar or even identical final expression using quite different starting points.

3　Examples for effective Hamiltonians

3.1　The Heisenberg exchange

The Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian [24–26] is a model Hamiltonian which is one of the simplest and most widely used Effective Hamiltonian. The Heisenberg Hamiltonian is a model that can describe interactions between unpaired electrons (belonging to metal atoms or organic radicals) localized on spatially separated atomic centers or groups of atoms constituting a molecule. Such a model is of considerable importance not only in the understanding of the electronic structure and properties of single molecule magnets (SMMs) but also for the design of molecules capable of showing a high-spin ground state. The Heisenberg-Dirac-van Vleck Hamiltonian reads

$$\hat{H}_{\text{Heisenberg}} = -2J_{ab}\hat{\mathbf{S}}_a \cdot \hat{\mathbf{S}}_b. \tag{55}$$

It is an effective Hamiltonian that works in the basis of spin states of the interacting sites and contains the adjustable parameter J_{ab} that is determined by fitting magnetization data (or other magnetic measurements). The task at hand is to elucidate how this parameter can be understood and also quantitatively calculated in terms of first-principles electronic structure theory.

3.1.1　Partitioning of the Hamiltonian and definition of Model space

Consider the simplest valence space made up of two electrons of opposite spin on centers A and B that are spatially separated. The Hilbert space of these two electrons in two orbitals is spanned by the Slater determinants

$$\left\{ |a\bar{b}\rangle, \, |\bar{a}b\rangle, \, |a\bar{a}\rangle, \, |b\bar{b}\rangle \right\},$$

where a and b refer to the valence local orbitals on centers A and B with a and $\bar{a}$ denoting the orbital at A occupied by an α or a β electron respectively. The determinants of the type

$\left\{|a\bar{b}\rangle \text{ and } |\bar{a}b\rangle\right\}$ belong to a configuration with one electron per center. These configurations are referred to as 'Neutral' configurations. On the other hand the centers with two (zero) electrons on a site are known as 'Ionic' configurations. The Ionic configurations can be expected to be high in energy as the two electrons occupy orbitals that are spatially closer and therefore suffer greater Coulomb repulsion compared to the Neutral configuration where they are spatially separated. Therefore, in local orbital basis, the low energy spectrum will be dominated by states made up dominantly of the Neutral configurations which will be well separated from states made up of Ionic configurations. The task of the Heisenberg Hamiltonian is then to describe the ground state of such systems in terms of the Neutral determinants only taking into account the effect of the Ionic states in an effective manner.

The full Hamiltonian in terms of the four determinants can be written as

$$
\begin{array}{c}
|a\bar{b}\rangle \\
|\bar{a}b\rangle \\
|a\bar{a}\rangle \\
|b\bar{b}\rangle
\end{array}
\begin{bmatrix}
0 & K_{ab} & t_{ab} & t_{ab} \\
K_{ab} & 0 & t_{ab} & t_{ab} \\
t_{ab} & t_{ab} & U & K_{ab} \\
t_{ab} & t_{ab} & K_{ab} & U
\end{bmatrix},
\tag{56}
$$

where we have taken the energy of the Neutral determinants as origin of energy. The matrix-elements of the Hamiltonian are as follows: the t_{ab} is the matrix-element $\langle a\bar{b}|\mathbf{H}|b\bar{b}\rangle$ and describes the movement of the electrons from site A to B, the direct exchange integral between orbitals a and b is represented by $K_{ab} = (ab|ba)$, and finally the Coulomb integral (electron-electron repulsion) on orbitals a and b is given by $U = (aa|aa) = (bb|bb)$.

The low energy spectrum of this Hamiltonian, i.e., one singlet and one triplet state, is dominated by the Neutral determinants whereas the higher energy states are dominated by the Ionic determinants. This intuition leads to a natural partition of the Hamiltonian given above into a model space and an outer space. The model space here is made of the two Neutral determinants whereas the outer space constitutes the two ionic determinants. The two determinants in the model space give rise to a singlet state and a triplet configuration which can be written as

$$
|T_0\rangle = \frac{1}{\sqrt{2}} \left(|a\bar{b}\rangle + |\bar{a}b\rangle \right),
\tag{57}
$$

$$
|S_N\rangle = \frac{1}{\sqrt{2}} \left(|a\bar{b}\rangle - |\bar{a}b\rangle \right),
\tag{58}
$$

where T_0 signifies the $M_S = 0$ component of the triplet state and the S_N signifies that the singlet is made up of neutral determinants. Note that both the singlet and triplet configurations are of gerade(g) symmetry. The outer space is made up of purely singlet configurations composed of ionic configurations which can be written in g and u symmetry combinations such as

$$
|S_I^g\rangle = \frac{1}{\sqrt{2}} \left(a\bar{a} - b\bar{b} \right),
\tag{59}
$$

$$
|S_I^u\rangle = \frac{1}{\sqrt{2}} \left(a\bar{a} + b\bar{b} \right).
\tag{60}
$$

In this basis, the above Hamiltonian given in Eq. (56) is transformed as follows

$$
\begin{array}{c}
|T_0\rangle \\
|S_N\rangle \\
|S_I^g\rangle \\
|S_I^u\rangle
\end{array}
\left[
\begin{array}{cc|cc}
-K_{ab} & 0 & 0 & 0 \\
0 & K_{ab} & 2t_{ab} & 0 \\
0 & 2t_{ab} & U+K_{ab} & 0 \\
0 & 0 & 0 & U+K_{ab}
\end{array}
\right]. \tag{61}
$$

Here, we have also partitioned the Hamiltonian into a model space which is the upper left block and the outer space which is the lower right one. Notice that the neutral singlet S_N only interacts with the ionic singlet of the same spatial symmetry i.e., S_I^g. There are a few important points that one realizes from the above form of the Hamiltonian which are as follows:

- Naturally, the triplet state T_0 does not interact with any of the other three states and therefore it does not change in energy. However, the energy of the triplet state is already lower than the singlet state by $2K_{ab}$ which means that in the absence of the interaction with the outer space (for, e.g., due to symmetry reasons), the ground state naturally tends towards a triplet state. This implies that the system can behave as a ferromagnet due the orthogonality of a and b orbitals which can be artificially or physically enforced.

- The singlet state, on the other hand, interacts with the ionic singlet state of gerade g symmetry. Therefore it is influenced by the outer space configurations. This always results in the stabilization of the lowest singlet state. In the case of large interaction between a and b given by $\langle a\bar{b}|\mathbf{H}|b\bar{b}\rangle$, this might invert the energetic ordering of the triplet and singlet states leading to a low spin singlet ground state and an antiferromagnetic coupling.

3.1.2 Derivation of the Effective Spin Hamiltonian via QDPT

Here we shall describe how the Heisenberg Hamiltonian given in Eq. (55) can be derived by using QDPT, as described in 2.5.1, and applied to the partitioned Hamiltonian given in Eq. (61). In order to see the expression for the "effective" interaction J_{ab}, it is instructive to investigate the g symmetry block of the Hamiltonian given in Eq. (62) [27],

$$
\begin{array}{c}
|T_0\rangle \\
|S_N\rangle \\
|S_I^g\rangle
\end{array}
\left[
\begin{array}{cc|c}
-K_{ab} & 0 & 0 \\
0 & K_{ab} & 2t_{ab} \\
0 & 2t_{ab} & U+K_{ab}
\end{array}
\right]. \tag{62}
$$

In order to derive the Heisenberg Hamiltonian, we first begin by defining the basis representations of the model space. The model space of the Heisenberg Hamiltonian contains only neutral configurations, i.e., configurations which show only isotropic spin-spin interaction. Therefore, we can adopt a more compact notation which only takes into account the spin degrees of freedom of the electron occupying orbitals a and b such as

$$
\{|\tfrac{1}{2}, M_{s_a}\rangle\} = \{|\uparrow\rangle_a, |\downarrow\rangle_a\}, \tag{63}
$$

$$
\{|\tfrac{1}{2}, M_{s_b}\rangle\} = \{|\uparrow\rangle_b, |\downarrow\rangle_b\}. \tag{64}
$$

Subsequently, the operators $\hat{\mathbf{S}}_a, \hat{\mathbf{S}}_b$ can be defined as

$$\hat{\mathbf{S}}_a = \hat{\mathbf{S}}_a^+ + \hat{\mathbf{S}}_a^- + \hat{\mathbf{S}}_a^z, \tag{65}$$

$$\hat{\mathbf{S}}_b = \hat{\mathbf{S}}_b^+ + \hat{\mathbf{S}}_b^- + \hat{\mathbf{S}}_b^z, \tag{66}$$

where the operators $\hat{\mathbf{S}}^+, \hat{\mathbf{S}}^-$ are the spin ladder operators and the $\hat{\mathbf{S}}^z$ gives the z component of the spin $\mathbf{S}$. Here, $\hat{\mathbf{S}}_\mathbf{a}$ and $\hat{\mathbf{S}}_\mathbf{b}$ operators act on model space representations $|\frac{1}{2}, M_{s_a}\rangle$ and $|\frac{1}{2}, M_{s_b}\rangle$ respectively.

Given this basis of the model space, operators and the Hamiltonian defined in Eq. (55), the matrix form of the model Hamiltonian can be written as

$$\begin{matrix} |\uparrow, \downarrow\rangle \\ |\downarrow, \uparrow\rangle \end{matrix} \begin{bmatrix} J_{ab} & -J_{ab} \\ -J_{ab} & J_{ab} \end{bmatrix} \tag{67}$$

with $\uparrow$ and $\downarrow$ representing the $M_s = \frac{1}{2}$ and $M_s = -\frac{1}{2}$ components of $S = \frac{1}{2}$ respectively. The value of J_{ab} can then be derived from QDPT based upon Eq. (62) at second order and takes the following form

$$2J_{ab} = 2K_{ab} - \frac{4t_{ab}^2}{U}. \tag{68}$$

Therefore, using the above expression for J_{ab}, the Heisenberg Hamiltonian can finally be derived as given in Eq. (55). Note that the operators $\hat{\mathbf{S}}_a$ and $\hat{\mathbf{S}}_b$ in Eq. (55) only describe the isotropic spin-spin interaction between the two electron spins assuming they are fixed on centers A and B respectively.

3.1.3   Physical interpretation of J_{ab}

Using the above derivation, one can analyze the physics described by the Heisenberg exchange J_{ab}, which is an effective parameter. As shown in Eq. (68), J_{ab} contains the effect of both the direct exchange K_{ab} and what is known as the kinetic exchange effect represented by the second term of Eq. (68):

$$\text{Direct Exchange:} \quad 2J_{ab}^{\text{direct}} = 2K_{ab}, \tag{69}$$

$$\text{Kinetic Exchange:} \quad 2J_{ab}^{\text{kinetic}} = -\frac{4t_{ab}^2}{U}. \tag{70}$$

Therefore, the nature of the exchange between sites A and B will be described by these two factors. The direct exchange K_{ab} has the effect of making J_{ab} more positive, i.e., stabilizing the high-spin state (triplet), whereas the kinetic exchange terms leads to a more negative J_{ab} and therefore stabilizes the low-spin state (singlet).

This also suggests how one can control and predict the nature of coupling by looking at the geometry (and hence the symmetry) of a given molecule. As described in the previous section if one orients the two magnetic orbitals a and b, such that their interaction is 0 due to symmetry, the term $\langle a\bar{b}|\mathbf{H}|b\bar{b}\rangle$ vanishes and the coupling is only due to the direct exchange K_{ab} which is always positive leading to a ferromagnetic coupling. In this manner, we can also predict new materials with the desired coupling and ground state. The "effective" Hamiltonian parameter

J_{ab} therefore results from a competition between these two contributions and shows how one can compress information efficiently without any loss in the described physics. Herein lies the power of effective and model Hamiltonian.

Here we have derived the Heisenberg Hamiltonian for the simplest case of two electrons in two valence orbitals. The Heisenberg Hamiltonian can of course be applied to multi-center molecules with more than one electron per center in which case the general form of the Hamiltonian is similar to Eq. (55) with summation over all nearest neighbors $\langle ab \rangle$. Note that in the case of a large number of interacting centers, a first principles treatment of the resulting molecular system becomes complicated due to the presence of a large number of open-shell electrons coupling to give a low-spin ground state. However, the physics of the problem remains largely the same.

A final point concerns the physics contained in the coupling term J_{ab} which is simple enough to describe in the case of two electrons. Such systems can be realized in Copper dimers and have been extensively studied by first principles calculations [28–30]. The detailed physical effects contained in J_{ab} turn out to be quite more complicated in reality and have been a subject of study for a long time [27].

3.2 The spin Hamiltonian in EPR and NMR spectroscopy

The spin Hamiltonian (SH) is a major asset in the analysis of magnetic resonance experiments. The massive simplification that the SH offers, is that it only contains the effective electron spin ($\hat{\mathbf{S}}$), the nuclear spins ($\hat{\mathbf{I}}$), and external magnetic fields ($\mathbf{B}$) but makes no explicit reference to electronic coordinates, molecular geometry, or any of the intricacies that render the application of the exact (relativistic) many particle Hamiltonian so difficult. The price to pay for this enormous simplification is that the SH contains adjustable parameters that are usually fitted to the results of magnetic measurements. A fairly standard SH may be written:

$$\hat{H}_{spin} = \beta \mathbf{B} \mathbf{g} \hat{\mathbf{S}} + \hat{\mathbf{I}} \mathbf{A} \hat{\mathbf{S}} + \hat{\mathbf{S}} \mathbf{D} \hat{\mathbf{S}} + \hat{\mathbf{I}} \mathbf{Q} \hat{\mathbf{I}} + ... \tag{71}$$

(β is the Bohr magneton). The individual terms are:

- $\beta \mathbf{B} \mathbf{g} \hat{\mathbf{S}}$ is the molecular Zeeman term that describes the interaction of the electron spin with an external magnetic field $\mathbf{B}$.

- $\hat{\mathbf{I}} \mathbf{A} \hat{\mathbf{S}}$ represents the hyperfine interaction that describes the interaction of an electron spin with the nuclear spin of a given nucleus.

- $\hat{\mathbf{S}} \mathbf{D} \hat{\mathbf{S}}$ is the zero-field splitting (ZFS) that describes the interaction of the unpaired electrons among themselves.

- $\hat{\mathbf{I}} \mathbf{Q} \hat{\mathbf{I}}$ is the quadrupole splitting that describes the interaction of the electric field gradient with the quadrupole moment of a nucleus.

All quantities $\mathbf{g}$, $\mathbf{A}$, $\mathbf{D}$ and $\mathbf{Q}$ are 3×3 tensors. Their elements are the adjustable parameters mentioned above. The SH acts on the space of spin functions

$$|SMIM_I\rangle = |SM\rangle \otimes |IM_I\rangle \tag{72}$$

that has the (small) dimension of $(2S+1)(2I+1)$. The matrix elements of the SH are straightforward to calculate using standard angular momentum operator algebra. The corresponding eigenvalue problems are of low dimension and can usually be solved with paper and pencil or very quickly numerically with a computer. The effective Hamiltonian approach enters the stage upon asking the question: "how are the SH parameters related to the actual electronic structure of my system?" Or, in other words, how do they relate to the (relativistic) eigenfunctions of the molecular Schrödinger equation. Below, we will derive the equation for $\mathbf{g}$ as an illustration of how the general argument proceeds.

The most straightforward connection is based on exploiting the partitioning method of section 2.3; see Eqs. (42), (43), and (53). To proceed from these equations, we need to define the nature of the 'A' and 'B' spaces and how we define the full Hamiltonian. Let us assume that we have solved the non-relativistic (BO) Schrödinger equation exactly, such that we know the entire spectrum of eigenstates:

$$\hat{H}_{\mathrm{BO}}\left|\Psi_I^{SM}\right\rangle = E_I \left|\Psi_I^{SM}\right\rangle. \tag{73}$$

Of course, this is entirely impractical, but we will still proceed along these lines for the sake of the conceptual argument. Since the BO Hamiltonian is spin-free, the total spin of the system and its projection on the z-axis are good quantum numbers and hence, we can label the eigenstates as $\left|\Psi_I^{SM}\right\rangle$. At the level of the BO Hamiltonian, these states are $(2S+1)$-fold degenerate. This degeneracy is then lifted by relativistic effects and external magnetic fields. If we are interested in the splittings of the 'magnetic sublevels' $M = S, S-1, ..., -S$ of the electronic ground state then it follows naturally to define the 'A' set as the $2S+1$ states belonging to the ground state multiplet (we assume that there are no other degeneracies than the spin degeneracies). The 'B' set then consists of the infinite number of excited states. The splittings induced by external magnetic fields and relativistic effects are relatively small – usually (but not always) on the order of only 1 cm^{-1} (roughly $5 \cdot 10^{-6}$ atomic units). On the other hand, the excited states are often > 5000–10000 cm^{-1} above the ground state. Hence, it is sensible to replace the unknown energy E in the effective Hamiltonian Eq. (43) by E_0, the energy of the ground state multiplet. Second, we need to define the full Hamiltonian operator. Since we are only interested in $\mathbf{g}$, we only need to consider two additional terms. One is the molecular Zeeman operator

$$\hat{H}_{\mathrm{Ze}} = \beta \mathbf{B} \sum_i \left(g_e \hat{\mathbf{s}}_i + \hat{\mathbf{l}}_i\right). \tag{74}$$

This operator consists of the spin-Zeeman ($g_e = 2.002319...$ is the free electron g-value) and orbital Zeeman operator. Note carefully that $\hat{\mathbf{s}}_i$ is the spin of the i'th electron, rather than the total spin $\hat{\mathbf{S}} = \sum_i \hat{\mathbf{s}}_i$. The angular momentum operator $\hat{\mathbf{l}}_i$ is referred to the global origin. The second term we need is the spin-orbit coupling (SOC) operator. In principle, this is a two-electron operator, but it can be reasonably well approximated by an effective one-electron

operator as given by Eq. (18). The operator $\mathbf{h}_i^{\mathrm{SOC}}$ can take many different forms like the SOMF operator mentioned in the introduction. One crude approximation is the effective nuclear charge Hamiltonian that has the form

$$\mathbf{h}_i^{\mathrm{SOC,ENC}} = \frac{\alpha^2}{2} \sum_A \frac{Z_A^{\mathrm{eff}}}{|\mathbf{R}_A - \mathbf{r}_i|^3} \hat{\mathbf{l}}_i^A, \tag{75}$$

where α is the fine structure constant, the sum A is over all nuclei in the system at positions $\mathbf{R}_A$ with effective charges Z_A^{eff}. $\hat{\mathbf{l}}_i^A$ is the angular momentum operator of the i'th electron relative to the A'th nucleus. We now have to insert the full Hamiltonian

$$\hat{H} = \hat{H}_{\mathrm{BO}} + \hat{H}_{\mathrm{Ze}} + \hat{H}_{\mathrm{SOC}} \tag{76}$$

and wavefunctions $\left| \Psi_I^{SM} \right\rangle$ into the effective Hamiltonian and pick out terms that are bilinear in $\mathbf{B}$ and $\hat{\mathbf{S}}$ since those will define the g-tensor. The effective Hamiltonian is given by (see Eq. (53))

$$\left\langle \Psi_0^{SM} \middle| \hat{H}_{\mathrm{eff}} \middle| \Psi_0^{SM'} \right\rangle = \left\langle \Psi_0^{SM} \middle| \hat{H} \middle| \Psi_0^{SM'} \right\rangle - \sum_{I>0} \Delta_I^{-1} \left\langle \Psi_0^{SM} \middle| \hat{H} \middle| \Psi_I^{S'M''} \right\rangle \left\langle \Psi_I^{S'M''} \middle| \hat{H} \middle| \Psi_0^{SM'} \right\rangle, \tag{77}$$

where $\Delta_I = E_I - E_0$ is the energy difference between the I'th multiplet and the ground state at the level of the BO Hamiltonian. A little reflection will quickly reveal that:

- The only first-order term (first term on the right-hand side of Eq. (77)) comes from the spin-Zeeman term and equals the free electron g-value.

- In the infinite sum over excited states, only those terms with $S' = S$ can contribute since the orbital Zeeman operator is spin-independent and the spin-Zeeman operator does not couple the ground and excited states.

- Contributions to the g-tensor will only arise from cross terms between $\hat{H}_{\mathrm{Ze}}$ and $\hat{H}_{\mathrm{SOC}}$ since these are the only ones that have the correct bilinear structure in $\mathbf{B}$ and $\hat{\mathbf{S}}$

Thus, the relevant part of the effective Hamiltonian becomes

$$\left\langle \Psi_0^{SM} \middle| \hat{H}_{\mathrm{eff}} \middle| \Psi_0^{SM'} \right\rangle = \beta \mathbf{B} g_e \cdot \left\langle \Psi_0^{SM} \middle| \mathbf{S} \middle| \Psi_0^{SM'} \right\rangle$$
$$- \beta \mathbf{B} \sum_{I>0} \Delta_I^{-1} \left\{ \left\langle \Psi_0^{SM} \middle| \sum_i \hat{\mathbf{h}}_i^{\mathrm{SOC}} \hat{\mathbf{s}}_i \middle| \Psi_I^{S'M''} \right\rangle \left\langle \Psi_I^{S'M''} \middle| \sum_i \hat{\mathbf{l}}_i \middle| \Psi_0^{SM'} \right\rangle + \mathrm{c.c.} \right\}. \tag{78}$$

This is to be compared to the matrix element of the SH (focusing on the z-component)

$$\left\langle SS \middle| \beta B_z g_{zz} \hat{S}_z \middle| SS \right\rangle = \beta B_z g_{zz} S, \tag{79}$$

from which it readily follows that

$$g_{zz} = g_e - \frac{1}{S} \sum_{I>0(S'=S)} \Delta_I^{-1} \left\{ \left\langle \Psi_0^{SS} \middle| \sum_i \hat{h}_i^{\mathrm{SOC},z} \hat{s}_i^z \middle| \Psi_I^{SS} \right\rangle \left\langle \Psi_I^{SS} \middle| \sum_i \hat{l}_i^z \middle| \Psi_0^{SS} \right\rangle + \mathrm{c.c.} \right\}. \tag{80}$$

The generalization to all components of the g-tensor is straightforward with the aid of the Wigner-Eckart theorem, but the details would lead too far astray here. We note in passing that $\mathbf{g}$ is not symmetric. However, $\mathbf{g}^T\mathbf{g}$ behaves like a proper symmetric second-rank tensor and hence, in the EPR community it is common practice to refer to it as the g-tensor. Along the same lines, all parts of the SH can be derived.

3.3 The size-consistent self-consistent configuration interaction method

In this section, we will demonstrate that effective (in this case intermediate) Hamiltonian approaches are not only useful to derive effective, parameterized models, but that they can also pave the way for new and accurate electronic structure methods. The method that we have chosen to highlight in this respect is the 'size-consistent-self-consistent configuration interaction' (SC^2-CI) method of Malrieu and coworkers [31, 32]. It is an elegant way to derive a size-consistent electron correlation theory that is similar in spirit to the older coupled-electron pair approaches (CEPA) and might be viewed as a step towards full coupled cluster theory with single- and double excitations (CCSD). Let us re-iterate the principle of CI: we start from a reference determinant $|\Phi_0\rangle$ and expand the many-particle wavefunction in terms of excited determinants in which one-, two-, ... occupied spin-orbitals have been replaced by virtual orbitals,

$$|\Psi\rangle = |\Phi_0\rangle + \sum_{ia} C_a^i |\Phi_i^a\rangle + \tfrac{1}{4} \sum_{ijab} C_{ab}^{ij} |\Phi_{ij}^{ab}\rangle + |\Psi_{\mathrm{higher}}\rangle, \tag{81}$$

where $|\Psi_{\mathrm{higher}}\rangle$ collectively denotes triple-, quadruple- and higher substitutions. As explained in the introduction, in untruncated form, this ansatz leads to an exact solution of the many particle Schrödinger equation in the chosen one-particle basis. However, it is well-known that the most important substitutions in this expansion are the doubly excited determinants. Hence, it is tempting to truncate the ansatz to single- and double substitutions, thus defining the $|\Psi_{\mathrm{CISD}}\rangle$ wavefunction by setting $|\Psi_{\mathrm{higher}}\rangle = 0$. This is still a somewhat computationally manageable theory, since the number of single and double substitutions 'only' grows as the fourth power of system size and the solution of the CISD equations features $O(N^6)$ scaling.

3.3.1 A model system

In order to see what is wrong with this method, consider first a single H_2 molecule in a minimal basis set consisting only of the bonding σ and anti-bonding σ^* orbital. Neglecting the single substitutions, we only have two determinants: $|\Phi_0\rangle = |\sigma\bar{\sigma}|$, $|\Phi_\mathrm{D}\rangle = |\sigma^*\bar{\sigma}^*|$. In this basis, the CID matrix becomes

$$\mathbf{H}_A = \begin{matrix} \sigma\ \bar{\sigma} \\ \sigma^*\bar{\sigma}^* \end{matrix} \begin{bmatrix} 0 & K \\ K & \Delta \end{bmatrix}, \tag{82}$$

where $\Delta = \langle\Phi_\mathrm{D}|H|\Phi_\mathrm{D}\rangle - \langle\Phi_0|H|\Phi_0\rangle$ and $K = \langle\sigma\bar{\sigma}||\sigma^*\bar{\sigma}^*\rangle$. The solution of the eigenvalue equation gives the correlation energy as

$$E_{\mathrm{corr}} = \tfrac{1}{2}\left(\Delta - \sqrt{\Delta^2 + 4K^2}\right), \tag{83}$$

which is the exact solution. Now, consider adding a second H_2 molecule at infinite distance. In this case our many particle basis consists of the three determinants

$$\left|\Phi_0\right\rangle, \left|\Phi_{\mathrm{D}}^{A}\right\rangle, \left|\Phi_{\mathrm{D}}^{B}\right\rangle, \tag{84}$$

where superscripts in 'Φ_{D}^{A}' and 'Φ_{D}^{B}' denote locally excited H_2 molecules. This leads us to the Hamiltonian

$$\mathbf{H}_{A+B}^{\mathrm{D}} = \begin{array}{c} \left|\Phi_0^{A}\right\rangle\left|\Phi_0^{B}\right\rangle \\ \left|\Phi_{\mathrm{D}}^{A}\right\rangle\left|\Phi_0^{B}\right\rangle \\ \left|\Phi_0^{A}\right\rangle\left|\Phi_{\mathrm{D}}^{B}\right\rangle \end{array} \begin{bmatrix} 0 & K & K \\ K & \Delta & 0 \\ K & 0 & \Delta \end{bmatrix} \tag{85}$$

and hence the correlation energy

$$E_{\mathrm{corr}} = \tfrac{1}{2}\left(\Delta - \sqrt{\Delta^2 + 8K^2}\right), \tag{86}$$

which is clearly wrong, because for non-interacting H_2 molecules, the correlation energy should be exactly twice the monomer correlation energy. This severe shortcoming is known as a lack of 'size-consistency'. Electron correlation methods that are not size-consistent are next to useless in practice since they will give inconsistent results as a function of system size. Now, let us try to remedy the situation by including further (higher) substitutions. The first that comes to mind is the simultaneous pair substitution $\left|\Phi_{\mathrm{Q}}\right\rangle = \left|\Phi_{\mathrm{D}}^{AB}\right\rangle$, which gives the Hamiltonian including quadruple substitutions $\left|\Phi_{\mathrm{Q}}\right\rangle$:

$$\mathbf{H}_{A+B}^{\mathrm{DQ}} = \begin{array}{c} \left|\Phi_0^{A}\right\rangle\left|\Phi_0^{B}\right\rangle \\ \left|\Phi_{\mathrm{D}}^{A}\right\rangle\left|\Phi_0^{B}\right\rangle \\ \left|\Phi_0^{A}\right\rangle\left|\Phi_{\mathrm{D}}^{B}\right\rangle \\ \left|\Phi_{\mathrm{D}}^{A}\right\rangle\left|\Phi_{\mathrm{D}}^{B}\right\rangle \end{array} \begin{bmatrix} 0 & K & K & 0 \\ K & \Delta & 0 & K \\ K & 0 & \Delta & K \\ 0 & K & K & 2\Delta \end{bmatrix}. \tag{87}$$

Diagonalizing this Hamiltonian gives us the ground state energy for the $A+B$ system as

$$E_{\mathrm{corr}}^{A+B} = \left(\Delta - \sqrt{\Delta^2 + 4K^2}\right), \tag{88}$$

which is the expected value, i.e., $E_{\mathrm{corr}}^{A+B} = 2E_{\mathrm{corr}}^{A}$. It is an elementary, yet rewarding mathematical excise to demonstrate that the inclusion of the quadruple substitutions indeed restores the size consistency of the calculation. What can we learn from this model system? First of all, that truncated CI is not size-consistent and that it is essential to remedy this shortcoming. Second, that the inclusion of higher substitutions restores this size consistency. This was a trivial exercise in this model system. However, in a real system the number of triple-, quadruple- and even higher substitutions becomes overwhelming very quickly. Hence, it is necessary to develop approximations that approximately include the effect of the higher substitutions without explicitly including them.

This is precisely the idea of the SC^2-CI method: we use the concept and language of intermediate Hamiltonians to divide the many particle space into three subspaces:

- The main model space that consists of only the reference determinant.

- The intermediate or "buffer" space that consists of the single- and double substitutions.

- The "outer space" consisting of the triple and quadruple substitutions.

Clearly, the task at hand is to incorporate the effect of the higher substitutions in an approximate manner. The task at had is thus to derive an effective Hamiltonian that incorporates these effects. This will come in the form of a "dressed" CISD Hamiltonian matrix, the diagonalization of which yields a size-consistent result that approximately incorporates the effects of the triple and quadruple substitutions.

3.3.2   The model problem treated via intermediate Hamiltonian theory

Before we show the connection between intermediate Hamiltonian theory and the SC^2-CI equations, it is instructive to analyze the wavefunction of the above $A + B$ model system with quadruply excited configurations. The Hamiltonian for $A + B$ given above has the ground state wavefunction

$$|\Psi\rangle = C_0 |\Phi_0^A\rangle |\Phi_0^B\rangle - C_{\mathrm{D}_A} |\Phi_\mathrm{D}^A\rangle |\Phi_0^B\rangle - C_{\mathrm{D}_B} |\Phi_0^A\rangle |\Phi_\mathrm{D}^B\rangle + C_\mathrm{Q} |\Phi_\mathrm{D}^A\rangle |\Phi_\mathrm{D}^B\rangle . \tag{89}$$

It can be readily derived that the explicit form of this wavefunction is

$$|\Psi\rangle = \frac{X^2}{(1+X^2)} \left(|\Phi_0^A\rangle |\Phi_0^B\rangle - \frac{1}{X} |\Phi_\mathrm{D}^A\rangle |\Phi_0^B\rangle - \frac{1}{X} |\Phi_0^A\rangle |\Phi_\mathrm{D}^B\rangle + \frac{1}{X^2} |\Phi_\mathrm{D}^A\rangle |\Phi_\mathrm{D}^B\rangle \right) \tag{90}$$

with $X = (2K + \sqrt{4K^2 + \Delta^2})/\Delta$. The products of the monomer wavefunctions occurring in this equation should be understood as being properly antisymmetrized. Importantly, it follows from Eq. (90) that the coefficient of the quadruply-excited configuration C_Q is exactly a product of the coefficient of the two doubly-excited ones C_{D_A} and C_{D_B}. This suggests a path towards a simplification that includes the higher order excitations without explicitly including them and hence towards the SC^2-CI formulation.

First, we begin by writing the CIDQ problem with a linearly parametrized function given in Eq. (89). The eigenvalue equation then is written as

$$\mathbf{H} |\Psi\rangle = E |\Psi\rangle , \tag{91}$$

$$\mathbf{H} |\Psi_\mathrm{HF}\rangle + \mathbf{H} |\Psi_\mathrm{D}\rangle + \mathbf{H} |\Psi_\mathrm{Q}\rangle = E\big(|\Psi_\mathrm{HF}\rangle + |\Psi_\mathrm{D}\rangle + |\Psi_\mathrm{Q}\rangle\big). \tag{92}$$

Here, the functions $|\Psi_\mathrm{HF}\rangle$, $|\Psi_\mathrm{D}\rangle$, and $|\Phi_\mathrm{Q}\rangle$ denote the reference, doubles, and quadruples component of the wavefunction respectively such as

$$|\Psi_\mathrm{HF}\rangle = C_\mathrm{HF} |\Phi_0^A \Phi_0^B\rangle , \tag{93}$$

$$|\Psi_\mathrm{D}\rangle = C_{\mathrm{D}_B} |\Phi_0^A \Phi_\mathrm{D}^B\rangle + C_{\mathrm{D}_A} |\Phi_\mathrm{D}^A \Phi_0^B\rangle = C_{\mathrm{D}_B} |\Psi_{\mathrm{D}_B}\rangle + C_{\mathrm{D}_A} |\Psi_{\mathrm{D}_A}\rangle , \tag{94}$$

$$|\Psi_\mathrm{Q}\rangle = C_\mathrm{Q} |\Phi_\mathrm{D}^A \Phi_\mathrm{D}^B\rangle = C_\mathrm{Q} |\Psi_{\mathrm{Q}_{AB}}\rangle . \tag{95}$$

The correlation energy E_{corr} is given by

$$\sum_{D \in D_A, D_B} C_D^2 E_{\text{corr}} = \langle \Psi_{\text{D}} | \mathbf{H} | \Psi_{\text{HF}} \rangle + \langle \Psi_{\text{D}} | \mathbf{H} | \Psi_{\text{D}} \rangle + \langle \Psi_{\text{D}} | \mathbf{H} | \Psi_{\text{Q}} \rangle. \tag{96}$$

From Eq. (96) it becomes clear that the task here is to avoid the last term $\langle \Psi_{\text{D}} | \mathbf{H} | \Psi_{\text{Q}} \rangle$ and at the same time obtaining a size-consistent solution. Here, we can leverage the understanding from the above discussion and make the following assumptions:

- The coefficients of quadruply excited configurations can be seen as products of doubly excited coefficients.

$$C_{\text{Q}} = C_{\text{D}_A} C_{\text{D}_B} \implies |\Psi_{\text{Q}}\rangle = \frac{1}{2} \sum_{\text{D}_X} \sum_{\text{D}_Y \neq \text{D}_X} C_{\text{D}_X} C_{\text{D}_Y} |\Psi_{\text{D}_X}\rangle.$$

- The matrix-elements between the doubles and quadruples $\langle \Psi_{\text{D}_X} | \mathbf{H} | \Psi_{\text{Q}_{AB}} \rangle$ have the same magnitude as that between the Φ_{HF} and doubles, i.e.

$$\langle \Phi_{\text{D}_X} | \mathbf{H} | \Phi_{\text{D}_X} \Phi_{\text{D}_Y} \rangle = \langle \Phi_{\text{HF}} | \mathbf{H} | \Psi_{\text{D}_Y} \rangle. \tag{97}$$

These two assumptions are exact in the case of two non-interacting molecules A and B. With these two assumptions, we can then simplify the expression for the correlation energy Eq. (96) such that

$$\langle \Psi_{\text{D}_X} | \mathbf{H} | \Psi_{\text{Q}} \rangle = \frac{1}{2} \sum_{\text{D}_Z} \sum_{\text{D}_Y \neq \text{D}_Z} C_{\text{D}_Z} C_{\text{D}_Y} \langle \Psi_{\text{D}_X} | \mathbf{H} | \Phi_{\text{D}_Z} \Phi_{\text{D}_Y} \rangle = \frac{1}{2} C_{\text{D}_X} \sum_{\text{D}_Y} C_{\text{D}_Y} \langle \Psi_{\text{D}_X} | \mathbf{H} | \Phi_{\text{D}_X} \Phi_{\text{D}_Y} \rangle, \tag{98}$$

$$\langle \Psi_{\text{D}_X} | \mathbf{H} | \Phi_{\text{D}_X} \Phi_{\text{D}_Y} \rangle = \langle \Psi_{\text{HF}} | \mathbf{H} | \Psi_{\text{D}_Y} \rangle, \implies \langle \Psi_{\text{D}_X} | \mathbf{H} | \Psi_{\text{Q}} \rangle = C_{\text{D}_X} E_{\text{corr}}.$$

Using this result and substituting it in Eq. (91) we finally get the coupled electron pair approximation of type 0 (CEPA-0) equations which are given by

$$C_{\text{D}_X} E = \langle \Psi_X | \mathbf{H} | \Psi_{\text{HF}} \rangle + \langle \Psi_X | \mathbf{H} | \Psi_{\text{D}} \rangle + C_{\text{D}_X} E_{\text{corr}}, \tag{99}$$

$$C_{\text{D}_X} E_{\text{HF}} = \langle \Psi_X | \mathbf{H} | \Psi_{\text{HF}} \rangle + \langle \Psi_X | \mathbf{H} | \Psi_{\text{D}} \rangle. \tag{100}$$

Hence, we recover a size-consistent form of CID without actually physically including the quadruply excited configurations.

Now looking at Eq. (99) one can show that it can also be written in an equivalent form in terms of a modification of the doubles part of the Hamiltonian. In fact, one can show that in our model system $\mathbf{H}_{A+B}^{\text{D}}$ above, if one replaces the diagonal energies of the doubly excited configurations Δ with an equivalent 'dressed' diagonal energy $\tilde{\Delta}$ given by

$$\tilde{\Delta} = \Delta + \frac{1}{2}\left(\Delta - \sqrt{\Delta^2 + 4K^2}\right) = \Delta + E_{\text{corr}}^A = \Delta + \frac{1}{2}E_{\text{corr}}^{A+B} \tag{101}$$

then the CID matrix looks like an intermediate effective Hamiltonian obtained by a diagonal 'dressing' of the intermediate space of the CID Hamiltonian

$$\tilde{\mathbf{H}}^{\mathrm{D}}_{A+B} = \begin{matrix} |\Phi_0^A\rangle |\Phi_0^B\rangle \\ |\Phi_{\mathrm{D}}^A\rangle |\Phi_0^B\rangle \\ |\Phi_0^A\rangle |\Phi_{\mathrm{D}}^B\rangle \end{matrix} \begin{bmatrix} 0 & K & K \\ K & \tilde{\Delta} & 0 \\ K & 0 & \tilde{\Delta} \end{bmatrix}. \tag{102}$$

This diagonally dressed Hamiltonian is exactly equivalent to the CEPA-0 equations and gives the expected correct Energy, i.e.,

$$\tilde{\mathbf{H}}^{\mathrm{D}}_{A+B} |\Psi\rangle = \tilde{E}^{\mathrm{D}}_{A+B}|\Psi\rangle, \tag{103}$$

$$\tilde{E}^{\mathrm{D}}_{A+B} = E^{\mathrm{DQ}}_{A+B} = \left(\Delta - \sqrt{\Delta^2+4K^2}\right) = 2E_A. \tag{104}$$

Therefore, a size-consistent CID Hamiltonian can be thought of as an intermediate Hamiltonian with a single configuration $|\Psi_{\mathrm{HF}}\rangle$ in the model space with all the doubles $|\Psi_{\mathrm{D}}\rangle$ being treated in the intermediate space and with the quadruples being the out-of-space configurations. Hence, in this sense, a size-consistent SC^2-CI consists of a state-specific (i.e., dependent on the specific model space $|\Psi_{\mathrm{HF}}\rangle$) dressing of the intermediate space configurations.

3.3.3 General case using intermediate effective Hamiltonians

In the previous section, we highlighted the basic idea of the role of intermediate Hamiltonian theory in the derivation of the SC^2-CI equations for a model system. Here we derive the equations for SC^2-CI in the general case following along the same steps as described above. In the general case, the model space will consist of the 0'th order wavefunction Ψ_0 and all the doubly excited configurations with respect to Ψ_0 given by Ψ_{D} make up the buffer space. The outer space will be made up of the quadruply excited configurations. This results in the same Schrödinger equation as before

$$\hat{H} |\Psi_0\rangle + \hat{H} |\Psi_{\mathrm{D}}\rangle + \hat{H} |\Psi_{\mathrm{Q}}\rangle = E\big(|\Psi_0\rangle + |\Psi_{\mathrm{D}}\rangle + |\Psi_{\mathrm{Q}}\rangle\big). \tag{105}$$

The goal here is to devise a diagonal dressing $\langle\Psi_{\mathrm{D}_X}|\tilde{\mathbf{V}}|\Psi_{\mathrm{D}_X}\rangle$ such that the intermediate Hamiltonian $\tilde{\mathbf{H}}$ given in Eq. (107) is size-consistent. This dressing is defined by the following equations

$$\tilde{\mathbf{H}} = \mathbf{P} \cdot \mathbf{H} \cdot \mathbf{P} + \tilde{\mathbf{V}}, \tag{106}$$

$$\sum_{\mathrm{D}_I} \tilde{C}_I \langle\Psi_X|\tilde{\mathbf{H}}|\Psi_{\mathrm{D}_I}\rangle = E\tilde{C}_X, \tag{107}$$

$$\sum_{\mathrm{D}_I} \tilde{C}_I \langle\Psi_X|\mathbf{H}|\Psi_{\mathrm{D}_I}\rangle + \sum_{Q_J} \tilde{C}_J \langle\Psi_X|\mathbf{H}|\Psi_{Q_J}\rangle = E\tilde{C}_X. \tag{108}$$

For this we proceed similarly to the previous case with the same two assumptions as before but we shall be careful about the indices here. The main task is the derivation of the last term on the LHS of Eq. (108). Using the assumption that the coefficients of the quadruples can be

expressed as products of the coefficients of the doubles (Eq. (98)), we can simplify the dressing $\langle \Psi_{\mathrm{D}_X} | \tilde{\mathbf{V}} | \Psi_{\mathrm{D}_X} \rangle$ as shown below

$$\langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Psi_Q \rangle = \frac{1}{2} \sum_{\mathrm{D}_Z} \sum_{\mathrm{D}_Y} C_{\mathrm{D}_Z} C_{\mathrm{D}_Y} \langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Phi_Z^{\mathrm{D}} \Phi_Y^{\mathrm{D}} \rangle \,, \tag{109}$$

$$\langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Psi_Q \rangle = C_{\mathrm{D}_X} \sum_{\mathrm{D}_Y \in \mathcal{D}_{\mathrm{D}_X}} C_{\mathrm{D}_Y} \langle \Psi_0 | \mathbf{H} | \Psi_{\mathrm{D}_Y} \rangle \,, \tag{110}$$

$$\langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Psi_Q \rangle = C_{\mathrm{D}_X} \langle \Psi_{\mathrm{D}_X} | \tilde{\mathbf{V}} | \Psi_{\mathrm{D}_X} \rangle \,, \tag{111}$$

$$\langle \Psi_{\mathrm{D}_X} | \tilde{\mathbf{V}} | \Psi_{\mathrm{D}_X} \rangle = \sum_{\mathrm{D}_Y} C_{\mathrm{D}_Y} \langle \Psi_0 | \mathbf{H} | \Psi_{\mathrm{D}_Y} \rangle - \sum_{Y \notin \mathcal{D}_{\mathrm{D}_X}} C_{\mathrm{D}_Y} \langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Psi_{\mathrm{D}_Y} \rangle \,, \tag{112}$$

$$\langle \Psi_{\mathrm{D}_X} | \tilde{\mathbf{V}} | \Psi_{\mathrm{D}_X} \rangle = E_{corr} - \sum_{\mathrm{D}_Y \notin \mathcal{D}_{\mathrm{D}_X}} C_{\mathrm{D}_Y} \langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Psi_{\mathrm{D}_Y} \rangle \,. \tag{113}$$

Here 'D_X' and 'D_Y' collectively denote a 4-tuple of indices (i, j, a, b) that denote double substitutions from occupied orbitals i and j to virtual orbitals a and b. Importantly, the summation over D_Y in the above equations is over those doubles that are 'disconnected' $\mathrm{D}_Y \in \mathcal{D}_{\mathrm{D}_X}$ with respect to the doubly excited configuration Ψ_{D_X}. The 'disconnected' refers to two tuples (i, j, a, b) and (k, l, c, d) where no index in the first tuple is identical to any index in the second tuple. This is a direct consequence of the Pauli exclusion principle since the quadruply substituted determinant is written as a product of doubly substituted. Hence, after performing a given double substitution, the second double substitution will only lead to a non-zero result if the spin-orbital that is depopulated by the second substitution is not already empty or the virtual orbital that is populated by the substitution is not already populated. This is only the case if no index is repeated. Substitutions that violate this requirement are known as 'exclusion principle violating' (EPV) terms. Therefore, the final expression of the dressing with the correct consideration of the EPV terms is as follows:

$$\langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Psi_0 \rangle + \langle \Psi_{\mathrm{D}_X} | \mathbf{H} | \Psi_{\mathrm{D}} \rangle + \tilde{C}_{\mathrm{D}_X} \left(E_{corr} - \Delta_{\mathrm{D}_X}^{\mathrm{EPV}} \right) = \tilde{C}_{\mathrm{D}_X} \left(E_{\mathrm{HF}} + E_{\mathrm{corr}} \right) . \tag{114}$$

The last thing to do is to derive the expression for the EPV terms of the diagonal dressing $\Delta_{\mathrm{D}_X}^{\mathrm{EPV}}$. Note that now the dressing becomes dependent on the doubly excited configuration Ψ_{D_X} which makes the result dependent on orbitals i, j, a, b which are the four orbitals involved in the double substitution $|\Psi_{\mathrm{D}_X}\rangle = E_i^a E_j^b |\Psi_0\rangle$. The expression for the EPV term may be written as

$$\Delta_X^{\mathrm{EPV}} = \sum_{klcd \in ijab} C_{\mathrm{D}_Y} \langle \Psi_0 | \mathbf{H} E_k^c E_l^d | \Psi_0 \rangle \,. \tag{115}$$

The EPV terms enumerated by considering the number of ways, in which one-, two-, three- or all four indices in the two tuples can coincide. There are four total different type of tuples k, l, c, d which satisfy the rule $k, l, c, d \in i, j, a, b$ depending on one, two, three or four indices in common. The intermediate quantities required for these cases are as follows:

- One common occupied index i (analogously for virtual)

$$e_1(i) = \sum_{kcd} \langle \Psi_0 | \mathbf{H} E_k^d E_i^c | \Psi_0 \rangle \,, \tag{116}$$

- one occupied pair (i,j) common (analogous for virtual pairs)

$$e_2(i,j) = \sum_{cd} \langle \Psi_0 | \mathbf{H} E_j^d E_i^c | \Psi_0 \rangle \,, \tag{117}$$

- a triple of indices identical (i,j,a) common (analogous of i,a,b)

$$e_3(i,j,a) = \sum_{c} \langle \Psi_0 | \mathbf{H} E_j^c E_i^a | \Psi_0 \rangle \,, \tag{118}$$

- all four indices common

$$e_4(i,j,a,b) = \langle \Psi_0 | \mathbf{H} E_j^b E_i^a | \Psi_0 \rangle \,. \tag{119}$$

Using these intermediate quantities, we can finally write general equations for the full SC^2-CISD as follows [31, 32]

$$
\begin{aligned}
\Delta_{\mathrm{D}X}^{\mathrm{EPV}} = \quad & e_1(i) + e_1(j) + e_1(a) + e_1(b) \\
& + e_2(i,j) + e_2(i,a) + e_2(i,b) + e_2(j,a) + e_2(j,b) + e_2(a,b) \\
& + e_3(i,j,a) - e_3(i,j,b) - e_3(i,a,b) - e_3(j,a,b) \\
& + e_4(i,j,a,b).
\end{aligned}
\tag{120}
$$

Thus, we have the general SC^2-CISD equations which include the correct contributions resulting from a careful consideration of the spurious EPV terms.

3.3.4 Further generalization and connection to Coupled Cluster Theory

The SC^2-CI represents a logical progression from the highly flawed CISD method towards a more accurate and size-consistent theory. It exactly restores size consistency by taking care of all EPV terms. However, it still has one significant shortcoming: the lack of unitary non-invariance. The Hartree-Fock wavefunction and even the CISD wavefunction is invariant under unitary transformations of the occupied or virtual orbitals among themselves. The SC^2-CI, owing to the way the higher substitutions are incorporated, does not have this property. Again, this is quite problematic for chemical applications of this theory. However, if one takes inspiration from this development, it is not difficult to envision how one can work around this problem. In fact, with some contemplation, one could arrive at the conclusion that the essential feature is to approximate higher substitutions as products of lower substitutions. Thus triples are products of singles- and doubles, quadruples arise from products of doubles with other doubles etc. The easiest way to formalize this, is to define the n-fold substitution operators $\hat{T}_n$:

$$\hat{T}_1 = \sum_{ia} t_a^i a_a^\dagger a_i \quad \hat{T}_2 = \tfrac{1}{4} \sum_{ijab} t_{ab}^{ij} a_a^\dagger a_i a_b^\dagger a_j \ \dots \tag{121}$$

Here, the t-amplitudes take the place of the CI coefficients. Thus, triple substitutions would be approximated as $\hat{T}_1 \hat{T}_2$, quadruples as $\hat{T}_2^2$ and so on. Importantly, these higher excitation do

not lead to additional wavefunction parameters. The singles and doubles amplitudes is all that is required. The simplest such theory is the QCISD theory of Pople and coworkers. It may be thought of as the simplest way to restore size consistency and unitary invariance in CISD. However, this is not how it historically came about. In fact, one can generalize the idea of using products of excitation operators in a beautiful way by using the coupled cluster ansatz briefly mentioned in the introduction, in which the many-particle wavefunction is written as an exponential

$$|\Psi\rangle = \exp(\hat{T}) |\Phi_0\rangle , \text{ with } \hat{T} = \hat{T}_1 + \hat{T}_2 + ... \tag{122}$$

Expanding the exponential leads to

$$\exp(\hat{T}) = \hat{1} + \hat{T} + \tfrac{1}{2}\hat{T}^2 + ... = \hat{1} + \hat{T}_1 + \hat{T}_2 + \tfrac{1}{2}\hat{T}_1^2 + \hat{T}_1\hat{T}_2 + \tfrac{1}{2}\hat{T}_2^2 + ... \tag{123}$$

Thus, all products of excitations are automatically included. It can readily be shown that the theory remains size consistent at any truncation level of the cluster operator. There would be much more to say about coupled cluster theory. However, here we only wanted to illustrate that physical reasoning based on effective Hamiltonians can lead in a natural way to its formulation. Today, coupled cluster theory is a mainstay of quantum chemistry and perhaps the most advanced and most successful wavefunction-based electronic structure method in existence.

3.4 Ab initio ligand field theory

3.4.1 Ligand field theory

The analysis of experimental results like optical absorption spectra shows that the low-energy states of many mononuclear transition metal complexes can be qualitatively understood as linear combinations of a certain set of Slater determinants. They all share the same doubly occupied MOs (ligand orbitals and core orbitals on the metal) and have different occupations of a set of 5 MOs that resemble the d orbitals of free transition metal atoms or ions. For simplicity, these MOs are also called d orbitals with the understanding that they are partially delocalized onto the ligands. Ligand field theory (LFT) is a parametrization of an effective Hamiltonian that describes this manifold of 'ligand field states' in terms of intuitively appealing parameters.

The form of the model can be derived as follows [33]: Within the Slater determinant basis introduced above, one can replace the BO Hamiltonian H (apart from a constant energy shift) by the effective Hamiltonian

$$H^{\text{eff}} = \sum_{i\in d} F_i^{\text{core}} + \sum_{i<j\in d} \frac{1}{r_{ij}}, \tag{124}$$

where

$$F^{\text{core}} = h + \sum_i (2J_i - K_i). \tag{125}$$

Note that the i in Eq. (124) denotes electrons in d orbitals, while i in Eq. (125) denotes doubly occupied orbitals. J_i and K_i in Eq. (125) are Coulomb and exchange operators. This means

that this effective Hamiltonian describes the movement of the d electrons in the mean field of the closed-shell core and ligand orbitals.

For constructing the matrix representation of the effective Hamiltonian Eq. (124) in the basis of all Slater determinants introduced above, one needs all one-electron integrals $F_{pq}^{\mathrm{core}} = \langle d_p | F^{\mathrm{core}} | d_q \rangle$ and two-electron integrals $(d_p d_q | d_r d_s)$. Since the core Fock operator is Hermitian, there are a total of 15 parameters arising from the one-electron integrals. Furthermore, there are (considering permutational symmetry) 120 independent two-electron integrals.

In the simplest ligand field model, one makes the assumption that the d orbitals have full spherical symmetry (i.e., they transform like the spherical harmonics belonging to quantum number $l = 2$). In this case, there are only 3 independent parameters in terms of which one can express all two-electron integrals. These parameters are either the Slater-Condon parameters F_0, F_2, F_4 or the Racah parameters A, B, C [33]. In ligand field theory, one usually denotes the one-electron part of the effective Hamiltonian as the one-electron ligand field matrix h_{pq}^{LFT} instead of a "core Fock operator". In high-symmetry situations, the number of parameters is highly reduced. For example, in tetrahedral or octahedral complexes, h_{pq}^{LFT} is fully determined (apart from an irrelevant constant energy shift) by a single number: the ligand field splitting Δ (often also denoted by $10Dq$), which is the orbital energy difference between the $e_{(g)}$ and the $t_{2(g)}$ orbital sets.

Traditionally, the parameters of the model are fitted to experimental data like electronic excitation energies, thermochemical data, EPR spectra, or magnetization data. Particularly in low-symmetry situations (where all elements of h_{pq}^{LFT} appear as distinct parameters), this fit is often underdetermined. Furthermore, one is fitting quantities that depend nonlinearly on the ligand field parameters. This means that there can be many local minima in parameter space and the fit is not unique. Therefore, the extracted ligand field parameters are not well-defined and can possibly lack physical meaning.

One should also note that since the Slater determinant basis used in the definition of the ligand field model is far from being complete, it describes the true spectrum only approximately if Eqs. (124) and (125) are understood literally. Fitting to experimental data (or to ab initio effective Hamiltonians as described below) can go beyond this simple picture and lead to parameters that for example include the effect of electron correlation. They can be considered as "renormalized parameters" [34].

3.4.2 Ab initio ligand field theory

The ab initio ligand field theory (AILFT) approach is based on the observation that the matrix elements of the ligand field effective Hamiltonian are linear functions of the parameters of the model [35]. When combining all the parameters in a single vector $\mathbf{p}$, one can write this as

$$H_{IJ}^{\mathrm{LFT}}(\mathbf{p}) = \sum_k H_{IJ}^{\mathrm{LFT},k} p_k. \tag{126}$$

Combining I and J into a single compound index (such that the effective Hamiltonian becomes a vector), this can also be written in matrix-vector form,

$$\mathbf{H}^{\text{LFT}}(\mathbf{p}) = \mathbf{A}\mathbf{p}, \tag{127}$$

where the matrix $\mathbf{A}$ is defined as $A_{IJ,k} = H_{IJ}^{\text{LFT},k}$.

The basic idea of AILFT is now to construct an ab initio effective Hamiltonian $\mathbf{H}^{\text{eff}}$ that describes the same part of the electronic spectrum as the LFT model Hamiltonian. One then optimizes the parameters $\mathbf{p}$ such that the model Hamiltonian resembles the ab initio effective Hamiltonian as much as possible. This can be achieved by minimizing the sum of squared deviations of all matrix elements, i.e., $\sum_{IJ} \left(H_{IJ}^{\text{eff}} - H_{IJ}^{\text{LFT}}(\mathbf{p}) \right) \overset{!}{=} \min$ (least-squares fitting). Since the matrix elements are linear functions of the parameters, this problem has a unique solution that is given by [36, 37]

$$\mathbf{p} = \mathbf{A}^{+}\mathbf{H}^{\text{eff}}, \tag{128}$$

where $\mathbf{A}^{+}$ is the Moore-Penrose pseudoinverse of $\mathbf{A}$. If the number of effective Hamiltonian matrix elements is larger than the number of parameters (which is usually the case), the pseudoinverse can be written as $\mathbf{A}^{+}=(\mathbf{A}^{T}\mathbf{A})^{-1}\mathbf{A}^{T}$. Inserting this into Eq. (128), one arrives at

$$\mathbf{p} = (\mathbf{A}^{\text{LFT}})^{-1}\mathbf{b}^{\text{LFT}}, \tag{129}$$

$$A_{kl}^{\text{LFT}} = \sum_{IJ} H_{IJ}^{\text{LFT},k} H_{IJ}^{\text{LFT},l}, \tag{130}$$

$$b_{k}^{\text{LFT}} = \sum_{IJ} H_{IJ}^{\text{LFT},k} H_{IJ}^{\text{eff}}. \tag{131}$$

These are the equations derived in the original description of the AILFT approach [35]. This ab initio approach for obtaining ligand field parameters is distinguished from traditional approaches by the fact that the model is linear (i.e., the fit is unique) and that the system is not underdetermined. This is because the full effective Hamiltonian provides much more information than just the energies.

The most straightforward ab initio effective Hamiltonian that can be used in the AILFT context is the CASCI Hamiltonian, where the metal d orbitals are chosen as active orbitals. In terms of its spectral resolution, it can be written as

$$\mathbf{H}_{\text{CASCI}} = \mathbf{C}_{\text{CASCI}}\mathbf{E}_{\text{CASCI}}\mathbf{C}_{\text{CASCI}}^{T}, \tag{132}$$

where $\mathbf{C}_{\text{CASCI}}$ is the matrix of CASCI coefficients and $\mathbf{E}$ is the diagonal matrix of energies. The problem in this case is that dynamic correlation, which is important for quantitative results, is missing. A straightforward way to incorporate dynamic correlation on top of a CASSCF calculation is 2nd order multireference perturbation theory (MRPT). Popular variants of MRPT are CASPT2 [38, 39] and NEVPT2 [40–42]. The standard version of these methods is state-specific, i.e., they are performed for each CASSCF root individually. A variant of AILFT based on state-specific NEVPT2 was introduced in which the ab initio effective Hamiltonian is in analogy to Eq. (132) defined as

$$\mathbf{H}_{\text{NEVPT2}}^{\text{eff}} = \mathbf{C}_{\text{CASCI}}\mathbf{E}_{\text{NEVPT2}}\mathbf{C}_{\text{CASCI}}^{T}. \tag{133}$$

By definition, this effective Hamiltonian has again simply the CASCI wavefunctions as eigenstates, while its energies include dynamic correlation at 2nd order in perturbation theory. A downside of this approach is that often large root-mean-square deviations (RMSDs) between the NEVPT2 energies and the energies of the fitted LFT model were observed, indicating that the LFT model is not well suited to parametrize the NEVPT2 effective Hamiltonian of Eq. (133). In contrast to this, there are also so-called multistate methods that can describe the dynamic-correlation-induced mixing of states in the model space. Recently, new versions of AILFT based on two such methods, the DCD-CAS(2) method [22, 23] and a Hermitian version of quasidegenerate NEVPT2 (HQD-NEVPT2) [43], were implemented and tested. It turns out that the possibility of state mixing can lead to better fits and lower RMSDs than at the NEVPT2 level. This leads to ligand field models that are closer to the physical picture provided by the ab initio calculations.

LFT has the advantage that it allows for the rationalization of complicated properties like excitation energies, EPR spectra, magnetization curves, and many other experimental results in terms of parameters whose behavior can be intuitively understood. In particular, the reduction of the size of the Racah parameters can be interpreted as a manifestation of the "nephelauxetic effect", i.e., the expansion of the size of the d orbitals due to covalency. A popular tool for analysis of the one-electron ligand-field matrix is the angular overlap model (AOM) [44,45]. In this case, the model parameters are e_σ and e_π, which are measures for the strength of σ and π bonding between the metal center and the ligand.

AILFT has been used in many studies over the last few years to rationalize the spectra and other properties of transition metal complexes. For example, it was used in the analysis of the magnetostructural correlations in pseudotetrahedral cobalt(II) complexes [46], the analysis of the ligand field of the azido ligand [47], and for the rationalization of experimental results on a cobalt single ion magnet [48]. Furthermore, AILFT was used to gain understanding of periodic trends in lanthanide [49,50] and actinide [50] ions and complexes.

For further information on AILFT, we refer to two recent review articles [51,52].

4 Conclusions

We hope that in this chapter, we have provided a useful entry point into the fascinating world of effective Hamiltonians. We have briefly touched upon many and diverse aspects of the subject. However, the serious student will need to consult the cited literature in order to work out any of the topics in full detail. Nevertheless, we hope that it came across that effective Hamiltonians are an incredibly versatile and powerful concept. They help us to conceptualize difficult electronic structure problems, they help us to connect in a clear and concise way to experimental reality and they may inspire us to develop more accurate electronic structure theories – to reiterate only a few possible applications. Clearly, the avenues that can be explored are nearly endless. Consequently, we hope that future generations of theoreticians will embrace effective Hamiltonians in their research and make ample use of the creative possibilities that their offer.

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