



Crystal–field parameters from ab initio calculations

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ARTICLE INFO

Article history:

Received 9 September 2008

Received in revised form 1 December 2008

Accepted 8 December 2008

Available online 24 December 2008

PACS:

71.70ch

71.15. – m

31.15. A –

71.23.An

Keywords:

Crystal–field, Ab initio, Lanthanide,

Rare-earth

ABSTRACT

We give a method for extracting an effective Hamiltonian from ab initio calculations that requires only the calculated energies for the model space and the part of the calculated eigenvectors that correspond to the model space. This method simplifies the extraction of phenomenological parameters that can be compared with experiment. We demonstrate the method with an ab initio calculation for d states, which is relevant to examining the $4f^{N-1}5d$ configurations of lanthanide and actinide ions.

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1. Introduction

The spectra of rare-earth ions in crystals are commonly analysed using *crystal–field* models. In these models an *effective Hamiltonian* is constructed within a *model space* for an isolate rare-earth ion (in a crystal). The model space most commonly consists of the $4f^N$ configuration but other configurations, such as $4f^{N-1}5d$, may also be considered. Parameters representing the various terms in the Hamiltonian, the Coulomb interaction between the electrons, spin–orbit interaction, crystal–field interaction, etc., are determined by fitting to observed energy levels, with ab initio calculations sometimes guiding the starting point [1].

Accurate ab initio calculations for the $4f^N$ and $4f^{N-1}5d$ configurations of rare-earth ion impurities in crystals are now becoming available [2,3]. There are several reasons why it would be useful to extract the commonly used effective Hamiltonian parameters from such calculations. The parameters give valuable insight into the interactions in these systems. For some purposes minor changes in the parameters would give better agreement with experiment, which could be crucial for calculating other properties of interest such as radiative or non-radiative transition rates. For many systems

it will be more practical to use ab initio calculations to determine crystal–field parameters for simple ions such as Ce^{3+} , and use those as input for effective Hamiltonian calculations in more complex systems.

In cases of high site symmetry, such as octahedral, only one crystal–field parameter is required to parameterize the crystal–field splitting of the 5d configuration of Ce^{3+} and in that case it is a simple matter to determine the parameter ($10Dq$ or B_0^4 depending on the convention used) from the calculated energies. However, for most site symmetries the number of crystal–field parameters is greater than or equal to the number of 5d energy levels, so fitting the parameters to the ab initio energy levels, as was done in Ref. [4], is not practical.

A better alternative is to construct a full effective Hamiltonian from the ab initio calculation, and then solve for the parameters. We show that the effective Hamiltonian that we require can be constructed from an ab initio calculation as long as we know the energies and the eigenvector components of the states within our model space in the ab initio wave-functions. An important point is that the full wave-function is not needed, only the components corresponding to the model space. We demonstrate the method with a simple example of a d-electron calculation.

2. Effective Hamiltonians

In this section we show how to construct an effective Hamiltonian using the eigenvalues and eigenvectors obtained from ab initio

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calculations. The theory of effective Hamiltonians has been extensively discussed by Hurtubise and Freed [5] and we have made use of some of these concepts in earlier papers [6,7].

The eigenstates of a quantum mechanical system may be written as

$$H\psi_i = E_i\psi_i \quad (i = 1, 2, \dots, \infty), \quad (1)$$

where E_i and ψ_i are the eigenvalues and eigenvectors, respectively. Usually, we are interested in a limited number of eigenvalues and their corresponding eigenvectors. This smaller space, of dimension M , is called the *model space*. Within this space we can construct an *effective Hamiltonian* H_{eff} which has eigenstates in the model space ϕ_i that yield energies identical to those for full Hamiltonian:

$$H_{\text{eff}}\phi_i = E_i\phi_i \quad (i = 1, 2, \dots, M). \quad (2)$$

It is important to note that the ϕ_i are not the same as the ψ_i , which may contain large admixtures of other functions. Furthermore, the choice of the ϕ_i is not unique. For example, we may use a model space consisting of $4f^N$ and $4f^{N-1}5d$ configurations of a trivalent lanthanide ion, but the “true” states contain mixtures of other orbitals on the ion and its ligands’.

The eigenstates ψ_i and ϕ_i may be expanded by a set of bases. We denote the complete set of bases as $|j\rangle$ ($j = 1, 2, \dots, \infty$). For convenience we may arrange our bases in such a way that, the first M bases are chosen to be the bases of the model space and the first M states are chosen to be those states whose major component bases may be written as

$$\psi_i = \sum_{j=1}^{\infty} |j\rangle V_{ji} \quad (3)$$

and its projection into the model space as

$$(\psi_P)_i = \sum_{j=1}^M |j\rangle V_{ji}. \quad (4)$$

Here $V = \{V_{ji}\}$ ($j, i = 1, 2, \dots, \infty$) is the matrix formed by all eigenvectors and $V_P = \{V_{ji}\}$ ($j, i = 1, 2, \dots, M$) the projection of the first M states into the model space. Note that the $(\psi_P)_i$ are generally not normalized or orthogonal and so are usually not the best choice for the model-space wave-functions, ϕ_i . It is not guaranteed that V_P is non-singular but for any practical systems we assume V_P is non-singular so that its inverse V_P^{-1} exists.

The set of original eigen-equations (Eq. (1)) can be written in matrix form as

$$HV = VE. \quad (5)$$

Here $E = \text{diag}(E_1, E_2, \dots, E_{\infty})$ is a matrix where the diagonal elements are the eigenvalues and all other elements are zero. We also define $E_P = \text{diag}(E_1, E_2, \dots, E_M)$ for later use.

A straightforward definition of a (non-Hermitian) effective Hamiltonian $H_{\text{eff}}^{\text{NH}}$ is

$$H_{\text{eff}}^{\text{NH}} = V_P E_P V_P^{-1}. \quad (6)$$

The eigen-equation

$$H_{\text{eff}}^{\text{NH}} V_P = V_P E_P \quad (7)$$

gives exactly the same eigenvalues as Eq. (5) for the first M states and the model-space eigenvectors are the columns of V_P . However, those eigenvectors are neither normalized nor orthogonal, and the effective Hamiltonian $H_{\text{eff}}^{\text{NH}}$ is not Hermitian, so this is not a suitable choice for comparison with a crystal-field Hamiltonian, which is explicitly constructed to be Hermitian.

Instead of using $H_{\text{eff}}^{\text{NH}}$, a Hermitian effective Hamiltonian H_{eff} may be constructed (e.g. Ref. [5] Eq. 2.11). Here we show that the construction requires only the energies and the part of the eigenvectors

that fall within the model space (V_P). We begin by constructing the orthonormal eigenvectors V_K :

$$V_K = ((V_P V_P^\dagger)^{-1})^{1/2} V_P. \quad (8)$$

It is noted that since V_P^{-1} is assumed to be non-singular, $(V_P V_P^\dagger)^{-1}$ exists and is positive-defined hermitian matrix, which is diagonalizable, and hence the square root of $(V_P V_P^\dagger)^{-1}$ is then well-defined (though there are, of course, arbitrary phases involved in solving for eigenvectors). Standard numerical methods may be used to calculate $(V_P V_P^\dagger)^{-1/2}$ directly.

The Hermitian effective Hamiltonian is therefore:

$$H_{\text{eff}} = V_K E_P V_K^{-1}. \quad (9)$$

We now have the effective eigenvalue equation (see Eq. (2)):

$$H_{\text{eff}} V_K = V_K E_P, \quad (10)$$

with a Hermitian effective Hamiltonian H_{eff} and orthonormal eigenstates:

$$V_K^\dagger V_K = 1_P. \quad (11)$$

Hence, with the M eigenvalues E_P and the components of their eigenvectors in the designated model space, V_P , we can use Eqs. (8) and (9) to construct a Hermitian effective Hamiltonian H_{eff} , whose eigenvectors are given by V_K . Extraction of the complete eigenstates is not required, which drastically simplifies the process.

Other properties of the system, such as dipole moments, may also be calculated using equations analogous to Eq. (9).

3. Solving for the effective Hamiltonian parameters

The “crystal-field” approach is to write a parameterized model-space Hamiltonian in terms of N_p parameters and operators:

$$H_{\text{eff}} = \sum_{\alpha=1}^{N_p} P_\alpha \mathbf{T}_\alpha. \quad (12)$$

Here the P_α are the parameters. The \mathbf{T}_α are the matrices of operators which represent the various interactions, such as the Coulomb interaction between the electrons, spin-orbit interaction, crystal-field interaction and so on.

If the operators span the model space we can expand the effective Hamiltonian exactly using elementary linear algebra. This is particularly simple if the operators are orthogonal, but if not, as long as they are linearly independent it is possible to construct a set of N_p equations

$$H_\beta = \text{tr}(\mathbf{T}_\beta^\dagger H_{\text{eff}}) \quad (13)$$

$$= \sum_{\alpha=1}^{N_p} A_{\beta\alpha} P_\alpha, \quad (14)$$

where

$$A_{\beta\alpha} = \text{tr}(\mathbf{T}_\beta^\dagger \mathbf{T}_\alpha). \quad (15)$$

Since A is non-singular when the set of N_p operators \mathbf{T}_α are linearly independent, we can solve for the parameters

$$P_\alpha = \sum_{\beta=1}^{N_p} (A^{-1})_{\alpha\beta} H_\beta = \sum_{\beta=1}^{N_p} (A^{-1})_{\alpha\beta} \text{tr}(\mathbf{T}_\beta^\dagger H_{\text{eff}}). \quad (16)$$

In most cases the crystal-field Hamiltonian will include only the operators representing the most important interactions in the expansion Eq. (12). If those operators do not form a complete set we

can still use Eq. (16) to calculate the strength parameters. However, there will be a residue since the expansion Eq. (12) will not give an exact fit.

4. Example

The methods described in the previous section could be applied to ab initio calculations for a range of physical systems. For simplicity we shall focus on an example relevant to systems with dilute transition metal or lanthanide ions, where the model space is composed of d or f orbitals on a particular ion. However, it would also be possible to apply the methods to concentrated systems, where magnetic anisotropy is of great concern. However, in such systems the transformation to the model space would be rather complex, since the calculation involves states that are not localized.

As an example we present the results from a density-functional calculation of the 3d orbital energies and wave-functions in VF_4^+ molecule. It is noted that this molecule itself is not of particular interest but is a simple example to demonstrate the method. This system is similar to the $5d^1$ problem for dilute Ce^{3+} ions in crystals. The calculations were done with the program Gaussian 2003 [8] and made use of density functionals. For illustrative purposes we have chosen a calculation with empty 3d orbitals merely to avoid the complication of dealing with partially occupied orbitals.

Since we want to illustrate our method for low symmetries we did not restrict the geometry to be tetrahedral. In the final optimized calculation there is a threefold symmetry axis approximately along the X-axis. However, the final geometry is close to tetrahedral, which is clear from the approximate two- and threefold degeneracies of the energies of the 3d states.

Energies for the 3d states are given in Table 1. The spin-orbit interaction was not included so there are five states of interest. The coefficients associated with the first two sets of Gaussian functions of d nature in the eigenvectors are also given. The eigenvector coefficients for these two sets differ by a factor of approximately 2, but the ratio depends on the energies of the states. In a crystal-field calculation the radial function are usually considered to be constant, but this restriction does not apply to the ab initio calculation. Consequently, we will obtain a slightly different effective Hamiltonian from the coefficients of each of the two sets of eigenvector components. However, in either case the calculated energies will be exactly reproduced.

Table 1

Calculated 3d energies and wave-functions for VF_4^+ from Gaussian 03 [8]. Energies are given in cm^{-1} relative to the configuration average. Note that there are 6 Gaussian orbitals rather than the 5 linearly independent orbitals expected for the 3d configuration. It is straightforward to transform each column of the wave-functions into a fivefold bases in terms of the spherical harmonic functions Y_m^2 . “d set 1” and “d set 2” contain the largest eigenvector coefficients of the five 3d states.

Energies	–3999	–3992	2650	2661	2680
d set 1					
5XX	–0.01697	0.03591	0.70002	–0.02945	–0.02230
5YY	–0.30254	–0.19785	–0.35082	–0.31824	0.37644
5ZZ	0.31950	0.16195	–0.34936	0.34768	–0.35414
5XY	0.43534	0.38356	–0.01154	–0.28186	0.28972
5XZ	–0.36104	0.45825	–0.05186	–0.24985	–0.30787
5YZ	–0.23534	0.32092	0.00906	0.45033	0.36917
d set 2					
6XX	–0.00813	0.01724	0.30897	–0.01291	–0.00979
6YY	–0.14544	–0.09515	–0.15443	–0.14010	0.16573
6ZZ	0.15368	0.07784	–0.15379	0.15307	–0.15591
6XY	0.20919	0.18432	–0.00509	–0.12382	0.12731
6XZ	–0.17349	0.22020	–0.02286	–0.10976	–0.13526
6YZ	–0.11317	0.15434	0.00402	0.19826	0.16254

Table 2

Crystal-field parameters for 3d states of VF_4^+ . Units are cm^{-1} .

Parameter	d set 1	d set 2
B_0^2	409	464
B_1^2	69	72
B_2^2	–514	–541
B_0^4	5748	5792
B_1^4	2615	2605
B_2^4	–6738	–6717
B_3^4	844	842
B_4^4	8321	8380

Since spin is ignored the effective crystal-field Hamiltonian may be written as

$$H_{\text{eff}} = \sum_{k=2,4} \sum_{q=-k}^k B_q^k C_q^{(k)}, \quad (17)$$

where the $C_q^{(k)}$ are spherical tensors [9]. The angular functions in Table 1 may be easily transformed into spherical tensors and we can use the eigenvector coefficients from either set of Gaussian functions to do the calculation.

In Table 2 we give crystal field parameters derived from the energies and eigenfunction of Table 1. Each column of Table 2 uses the eigenvector components from the corresponding section of Table 1.

The calculation was set up to restrict the geometry to C_{3v} and there is a threefold axis approximately along X. However, the expected twofold degeneracies are not exact due to rounding errors. The functions (or parameters) may be rotated to make the Z-axis the unique axis, so that to a good approximation we only have the three parameters B_0^2 , B_0^4 and B_3^4 , that we would expect for C_{3v} symmetry. Note that even these three parameters could not be determined from the energies (since there are only two energy differences) let alone the parameter set given in Table 2.

More sophisticated calculations, such as those in Ref. [3], optimize separately for each energy level. The method described here could still be used in those cases. There is no requirement for the original eigenvectors V to be orthonormal, so eigenvector components from different calculations may be combined to derive an effective Hamiltonian.

5. Conclusions

In this paper we have derived and demonstrated a simple method for extracting effective Hamiltonian parameters such as “crystal-field” parameters from ab initio calculations. Only the ab initio energies and eigenvector components corresponding to the states of interest are required. Details of the eigenvector components outside of the model space are not required. This method should be applicable to the analysis of a variety of ab initio calculations.

Acknowledgements

M.F.R. acknowledges support from City University of Hong Kong in the form of a Visiting Fellowship.

C.-K.D. acknowledges support of this work by the City University of Hong Kong Research Grant 9360123.

C.-K.D. and H.W.Z. acknowledge the National Science Foundation of China Grant No. 10874173 for financial support.

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