A many-body approach to crystal field theory

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A self-consistent many-body approach is proposed to build a first-principles crystal field theory, where crystal field parameters are calculated *ab initio*. Many-body theory is used to write the energy of the interacting system as a function of the density matrix of the noninteracting system. A variation of the energy with respect to the density matrix gives an effective Hamiltonian matrix that is diagonalized to determine the density matrix providing the lowest energy. The equations are written in terms of the Hopf algebra of functional derivatives with respect to external fermionic sources. This approach contains the many-body theory of Green functions as a special case and the usual crystal field theory as a first approximation. Therefore, it is expected to provide good results for strongly-interacting electron systems.

The many-body theory of realistic quantum systems uses two main methods: (i) the Green function method that gives good results for extended states such as metals and semiconductors and (ii) the diagonalization method, typically used in quantum chemistry, which describes efficiently localized systems and the splitting of degenerate states. The latter model is efficient to calculate the magnetism of rare earths and transition metal impurities in insulators, as well as of their optical and spectroscopic properties. However, the second method leads to the diagonalization of very large matrices for complex systems. Thus, an intermediate approach is desirable, where a small-size Hamiltonian is set up using effective parameters. The best-known example of this approach is the crystal-field or ligand-field method, which was extended by Kotani and coll. [1] to describe the interaction between a localized and an extended system. It gives good results for the calculation of x-ray absorption and photoemission spectroscopies.

The main drawback of this method is its use of parameters, which can be numerous in the case of low symmetry. The calculation of crystal field and Slater parameters in molecules and solids is a subject of continued interest [2–11], but they are not part of a general formalism and double counting of interactions is difficult to control. Moreover, the effect of the crystal field is not taken into account self-consistently.

In this paper, we propose a first-principles approach of the effective Hamiltonian method, based on the quantum field theory of correlated systems [12].

It was noticed a long time ago by Esterling and Lange [13] that the many-body solution of a degenerate or quasidegenerate system contains a loophole: among the various (quasi) degenerate states of the noninteracting system, only one will evolve towards the ground state of the interacting system, and it must be known in advance to set up the many-body calculation. Here we solve this problem by showing that the relevant state of the noninteracting system can be obtained by diagonalizing an effective Hamiltonian. Moreover, as shown in [12], the requirement of self-consistency imposes the use of density matrices instead of pure states. So, for a density matrix ρ, we calculate the total energy of the interacting system $E(\rho)$. To determine the density matrix ρ that minimizes the energy, we have to diagonalize an effective matrix which is determined by the Hopf-algebraic approach to many-body theory. Therefore, this method unifies the diagonalization method and the Green function method.

Total energy of the system – Standard many-body theory [14] enables us to write the total energy of an interacting system which evolves from a noninteracting system described by the density matrix ρ as

$$E(\rho) = \mathrm{tr}\Big(\rho S^{-1} T\big(H(0)\mathrm{e}^{-i\int_{-\infty}^{\infty} H^{\mathrm{int}}(t)\mathrm{d}t}\big)\Big), \quad (1)$$

where S is the S-matrix, T is the time-ordering operator and $H(t) = H_0(t) + H^{\mathrm{int}}(t)$ is the total Hamiltonian in the interaction representation, with

$$H_0(t) = \int \psi^\dagger(t,\mathbf{r}) h_0(\mathbf{r}) \psi(t,\mathbf{r})\mathrm{d}\mathbf{r},$$
$$H^{\mathrm{int}}(t) = \frac{e^2}{2}\int \frac{\psi^\dagger(t,\mathbf{r})\psi^\dagger(t,\mathbf{r}')\psi(t,\mathbf{r}')\psi(t,\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',$$

where $h_0(\mathbf{r}) = -\Delta/2m + U_N(\mathbf{r})$ is the one-body Hamiltonian operator for an electron in a nuclear potential $U_N(\mathbf{r})$.

Within the functional derivative approach to quantum field theory [15], this expression can be rewritten $E(\rho) = P(Z_\rho)$, where

$$P(Z_\rho) = \int \lim_{\mathbf{r}'\to\mathbf{r}} h_0(\mathbf{r}) \frac{\delta^2 Z_\rho}{\delta\bar\eta^+(x)\delta\eta^+(y)}\mathrm{d}\mathbf{r} + \int \frac{e^2}{2|\mathbf{r}-\mathbf{r}'|}\frac{\delta^4 Z_\rho}{\delta\bar\eta^+(y)\delta\bar\eta^+(x)\delta\eta^+(x)\delta\eta^+(y)}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',$$

where $x = (t,\mathbf{r})$, $y = (t,\mathbf{r}')$ and the right-hand side is taken for zero external sources. Z_ρ is the generating function of the Green functions. It is given by the expression $Z_\rho = \sum_{KL}\rho_{LK} Z_{KL}$, with ρ_{LK} the density matrix and

$$Z_{KL} = \langle K|S(\bar\eta^-,\eta^-)^{-1} S(\bar\eta^+,\eta^+)|L\rangle.$$

Here, $S(\bar\eta^\pm,\eta^\pm)$ is the S-matrix in the presence of fermionic external sources $\bar\eta^\pm$ and $\eta^\pm$ and $Z_{KL} = \mathrm{e}^{-iD} Z^0_{KL}$, where $D = D_+ - D_-$ and $D_\pm$ is the interaction term $\int_{-\infty}^{\infty} H^{\mathrm{int}}(t)\mathrm{d}t$ where the fields are replaced by functional derivatives with respect to the external sources $\bar\eta_\pm,\eta_\pm$. Finally, $Z^0_{KL} = \exp[-i\int \bar{\boldsymbol\eta}(x) G^0_0(x,y)\boldsymbol\eta(y)\mathrm{d}x\mathrm{d}y] N^0_{KL}$. In this equation, $\boldsymbol\eta$ is a two-dimensional vector with components η_+ and η_-, $G^0_0(x,y)$ is the 2x2 matrix

$$\begin{pmatrix} -i\langle 0|T\big(\psi(x)\psi^\dagger(y)\big)|0\rangle & -i\langle 0|\psi^\dagger(y)\psi(x)|0\rangle \\ i\langle 0|\psi(x)\psi^\dagger(y)|0\rangle & -i\langle 0|T^*\big(\psi(x)\psi^\dagger(y)\big)|0\rangle \end{pmatrix},$$

T^* is the anti-time-ordering operator and $N^0_{KL} = \langle K|{:}\exp\big[i\int\bar\eta_d(x)\psi(x) + \psi^\dagger(x)\eta_d(x)\mathrm{d}x\big]{:}|L\rangle$, with $\eta_d = \eta_+ - \eta_-$. The proof of these formulas can be found in [15].

To calculate N^0_{KL}, we must define precisely the states $|K\rangle$ and $|L\rangle$. The solution of the noninteracting Schrödinger equation provides one-electron orbitals $u_n(\mathbf{r})$ with energy ϵ_n. An orbital is called a core orbital if it is filled in all states $|K\rangle$ and $|L\rangle$, otherwise, it is called a valence orbital. The core orbitals are numbered from 1 to C, the valence orbitals from 1 to M. There are C electrons in the core orbitals and $N \le M$ electrons in the valence orbitals. For example, in the ion Cr^{3+}, there are $C = 18$ core orbitals and $N = 3$ electrons in the $M = 10$ orbitals of the degenerate 3d shell. The states are generated from the vacuum $|0\rangle$ by the action of creation operators $c^\dagger_n$ for core electrons and $v^\dagger_n$ for valence electrons as

$$\begin{aligned} |K\rangle &= v^\dagger_{i_N}\dots v^\dagger_{i_1} c^\dagger_C \dots c^\dagger_1 |0\rangle, \\ |L\rangle &= v^\dagger_{j_N}\dots v^\dagger_{j_1} c^\dagger_C \dots c^\dagger_1 |0\rangle, \end{aligned}$$

where i_k, j_k are valence orbitals (i.e. integers taken in the set $\{1,\dots,M\}$) ordered so that $i_1 < \cdots < i_N$ and $j_1 < \cdots < j_N$. A lengthy calculation yields

$$\begin{aligned} N^0_{KL} &= \prod_{k=1}^{C}(1+\bar\alpha_k\alpha_k) \\ &\quad\times \exp\Big(\sum_{n=1}^{M}\frac{\partial^2}{\partial\alpha_n\partial\bar\alpha_n}\Big)\bar\alpha_{j_1}\alpha_{i_1}\dots\bar\alpha_{j_N}\alpha_{i_N}, \end{aligned}$$

with $\bar\alpha_n = \int\bar\eta_d(x)u_n(x)\mathrm{d}x$ and $\alpha_n = \int u^\dagger{}_n(x)\eta_d(x)\mathrm{d}x$, where $u_n(x) = \mathrm{e}^{-i\epsilon_n t}u_n(\mathbf{r})$, $u^\dagger{}_n(x) = \mathrm{e}^{i\epsilon_n t}u^\dagger{}_n(\mathbf{r})$ and $x = (t,\mathbf{r})$.

Notice that, for vanishing sources (i.e. when $\eta^\pm = \bar\eta^\pm = 0$), $Z_{KL} = \delta_{K,L}$. To calculate $E(\rho)$, it is also possible to use the Galitskii-Migdal formula [16], but our expression for $E(\rho)$ allows for a more direct comparison with the standard equations of the crystal field theory.

Energy minimization – The minimization of $E(\rho)$ with respect to ρ is constrained by the fact that ρ must be Hermitian, nonnegative and with unit trace. To remove the trace condition, we use the fact that, for a general matrix ρ, $Z_\rho = \mathrm{tr}(\rho)$ for vanishing sources. So the trace condition is relaxed by writing the energy as $E(\rho) = P(Z_\rho)/Z_\rho$. The conditions of Hermiticity and nonnegativeness are relaxed by writing $\rho = b^\dagger b$, where b is now unconstrained. If we take the derivative of $E(\rho) = P(Z_\rho)/Z_\rho$ with respect to $b^\dagger$ and look for an extremum where $\partial E(\rho)/\partial b^\dagger = 0$ we obtain the equation $E(\rho)\partial Z_\rho/\partial b^\dagger = P(\partial Z_\rho/\partial b^\dagger)$ or, more explicitly $E(\rho)\sum_M b_{KM}Z_{ML} = \sum_M b_{KM}P(Z_{ML})$. For vanishing sources we have $Z_{ML} = \delta_{L,M}$ and this equation becomes $E(\rho)b = bP(Z)$, where Z is the matrix Z_{ML}.

To solve this, we diagonalize $P(Z)$. This gives us a unitary matrix U and a diagonal matrix z such that $E(\rho)b = bUzU^\dagger$, or $E(\rho)bU = bUz$.

To determine the general solution of this equation, we order the eigenvalues and eigenvectors of $P(Z)$ and we call e_0 the smallest eigenvalue. We put $R = bU$, and we assume that the lowest eigenvalue is d-fold degenerate. The general solution of $E(\rho)bU = bUz$ (i.e. $E(\rho)R = Rz$) giving the minimum energy is $E(\rho) = e_0$ and $R_{ij} = 0$ for $j > d$. Then $b = RU^\dagger$ and $\rho = UR^\dagger RU^\dagger$, where $R^\dagger R$ is an arbitrary Hermitian nonnegative d-dimensional matrix. At this stage, we can determine R by considering the symmetry of the system. The solution which gives the same weight to each eigenstate (and then the maximum symmetry) is $R^\dagger R = 1_d$. This determines the density matrix to be

$$\rho_{KL} = \frac{1}{d}\sum_{M=1}^{d} U_{KM}U^\dagger_{LM}, \tag{2}$$

where the factor $1/d$ was added to have $\mathrm{tr}(\rho) = 1$. The maximum symmetry can be broken by choosing another d-dimensional matrix $R^\dagger R$. For example, in a spherically symmetric system, the matrix $R^\dagger R$ can be chosen to select a specific spectroscopic term ${}^{2S+1}L$. In systems where the spin-orbit interaction is weak, we can select a given spin state. This can be useful to make self-consistent calculations of low-spin and high-spin transition metal ions.

The effective matrix – It remains now to determine the effective matrix $P(Z)$. We can obtain $P(Z)$ by noticing that $Z_\rho = \sum_{KL}\rho_{LK}Z_{KL}$ implies $Z_{KL} = \partial Z_\rho/\partial\rho_{LK}$. Therefore, the equation for Z_{KL} can be obtained from an equation for Z_ρ by a derivation with respect to ρ_{LK}.

The equation for Z_ρ is [12]

$$\partial Z_\rho = \sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\sum(-1)^{|D^n_{(1')}|}(D^n_{(1')}\partial W^1_\rho)(D^n_{(2')}Z_\rho), \tag{3}$$

where ∂ is a functional derivative with respect to an external source $\bar\eta^\pm(x)$ or $\eta^\pm(x)$. In fact, we need an infinite system of equations (the Green function hierarchy) obtained by taking the functional derivative of equation (3):

$$d\partial Z_\rho = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \sum (-1)^f (d_{(1)} D^n_{(1')} \partial W^1_\rho)(d_{(2)} D^n_{(2')} Z_\rho), \quad (4)$$

where $f = |D^n_{(1')}| + |d_{(2)}||D^n_{(1')}| + |d_{(2)}|$, d is a polynomial in the functional derivatives with respect to an external source $\bar\eta^\pm(x)$ or $\eta^\pm(x)$ and all quantities are taken for vanishing sources (i.e. $\bar{\boldsymbol\eta} = \boldsymbol\eta = 0$). In the rest of the discussion, we consider only the equation for ∂Z_ρ, the other equations being obtained through further functional derivatives, as for equation (4).

Taking the partial derivative of equation (3) with respect to ρ_{LK}, we obtain an equation for ∂Z_{KL}:

$$\partial Z_{KL} = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \sum (-1)^{|D^n_{(1')}|} \Big((D^n_{(1')} \partial W^1_{KL})(D^n_{(2')} Z_\rho) + (D^n_{(1')} \partial W^1_\rho)(D^n_{(2')} Z_{KL}), \quad (5)$$

where $W^1_{KL} = \partial W^1_\rho / \partial \rho_{LK}$. For the calculation of the partial derivative of W^1_ρ with respect to ρ_{LK}, it is necessary that a general value of ρ be used in W^1_ρ. In particular, ρ must not be assumed Hermitian or with unit trace. This implies the presence of terms such as $1/\mathrm{tr}(\rho)$ in W^1_ρ. Once the partial derivative is calculated, the condition $\mathrm{tr}(\rho) = 1$ can be restored to simplify W^1_{KL}. Notice that W^1_ρ is not linear in ρ, so W^1_{KL} depends on ρ. This dependence implies that the solution of the system of equations for ρ, Z_ρ and Z_{KL} must be solved self-consistently.

We are interested in the energy splitting due to the interaction. So we can remove the terms that are proportional to δ_{KL} because they just shift all eigenvalues by a constant term and do not modify the eigenvectors. To do that we write $Z_{KL} = Y_{KL} + (Z_\rho + \bar Y)\delta_{KL}$, with the boundary conditions $Y_{KL} = 0$ and $\bar Y = 0$ for vanishing external sources. Introducing this into equation (5), we obtain the following equation for Y_{KL}:

$$\partial Y_{KL} = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \sum (-1)^{|D^n_{(1')}|} \Big((D^n_{(1')} \partial V_{KL})(D^n_{(2')} Z_\rho) + (D^n_{(1')} \partial W^1_\rho)(D^n_{(2')} Y_{KL}) \Big), \quad (6)$$

where

$$V_{KL} = W^1_{KL} - \frac{\delta_{KL}}{\dim} \sum_K W^1_{KK},$$

with dim the dimension of the matrix W^1_{KL}.

Finally, the algorithm for the calculation of the density matrix ρ and the Green functions dZ_ρ is the following: (i) choose an initial density matrix ρ, (ii) calculate W^1_ρ and V_{KL}, (iii) use equation (4) to calculate the dZ_ρ you need for the calculation of the energy, (iv) calculate dY_{KL} for a given value of dZ_ρ and V_{KL}, (v) diagonalize $P(Y_{KL})$, (vi) deduce a new density matrix ρ_{new}, (vii) compare ρ_{new} and ρ, if convergence is not reached, go back to (ii) with a new ρ. Remark that steps (iii) and (iv) require the solution of an infinite system of equations. This system must be broken by some closure approximation of the Green function hierarchy and the resulting dZ_ρ and dY_{KL} are thus approximate. Notice also that another self-consistency loop can be introduced in the algorithm to calculate a self-consistent external potential, as was described in [12]. This will change the orbitals $u_n(x)$.

The crystal field equations – We must show that the present approach contains the standard crystal field equations as a first-order approximation. The functions we need to calculate $P(Y_{KL})$ are $\partial\partial' Y_{KL}$ with $\partial' = \delta/\delta\eta^+(y)$ and $\partial = \delta/\delta\bar\eta^+(x)$ and $\partial_1\partial_2\partial_3\partial_4 Y_{KL}$ with $\partial_4 = \delta/\delta\eta^+(y)$, $\partial_3 = \delta/\delta\eta^+(x)$, $\partial_2 = \delta/\delta\bar\eta^+(x)$ and $\partial_1 = \delta/\delta\bar\eta^+(y)$. If we solve iteratively equations (4) and (6) for $n = 0$ we obtain

$$\begin{aligned}
\partial\partial' Y_{KL} &= \partial\partial' V_{KL}, \\
\partial_1\partial_2\partial_3\partial_4 Y_{KL} &= \partial_1\partial_2\partial_3\partial_4 V_{KL} + (\partial_3\partial_4 V_{KL})(\partial_1\partial_2 W^1_\rho) \\
&\quad - (\partial_2\partial_4 V_{KL})(\partial_1\partial_3 W^1_\rho) + (\partial_1\partial_4 V_{KL})(\partial_2\partial_3 W^1_\rho).
\end{aligned}$$

A lengthy calculation shows that $P(Y_{KL})$ gives the same matrix as the standard crystal field theory.

The simplest example – As an example, we consider the case of one electron (N=1) that can occupy two orbitals (M=2). The density matrix is then of dimension 2. The matrix V_{KL} takes the form

$$V_{KL} = \begin{pmatrix} (\bar\alpha_1\alpha_1 - \bar\alpha_2\alpha_2)/2 & \bar\alpha_2\alpha_1 \\ \bar\alpha_1\alpha_2 & (\bar\alpha_2\alpha_2 - \bar\alpha_1\alpha_1)/2 \end{pmatrix} + \bar\alpha_1\alpha_1\bar\alpha_2\alpha_2 \begin{pmatrix} (\rho_{11} - \rho_{22})/2 & \rho_{12} \\ \rho_{21} & (\rho_{22} - \rho_{11})/2 \end{pmatrix}.$$

In particular, if the system is degenerate ($\rho_{11} = \rho_{22} = 1/2, \rho_{12} = \rho_{21} = 0$), the second term is zero and V_{KL} has only a term linear in $\bar\alpha$ and α.

We presented a first-principles self-consistent many-body approach to crystal field theory. Our approach contains by construction the many-body Green function theory as the case $N = M = 1$ and it contains the crystal field theory as a first order approximation. Thus, it is expected to provide good results in situations that are intermediate between the range of validity of these two limits, such as in strongly-interacting electron systems.

This method can be used more generally to calculate the splitting, due to interaction, of levels that are degenerate in the noninteracting system, for any quantum field theory. A interesting example is the application of this approach to the quantum electrodynamics of atoms, where its self-consistency should make it competitive with respect to the effective Hamiltonian methods proposed by Shabaev [17] and Lindgren [18].

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