A Product Basis Method for Calculating Dielectric Matrices

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Abstract

We present a method for calculating dielectric matrices of periodic systems. Unlike the conventional method which uses a planewave basis, the present method employs a product basis, which in the Linear Muffin Tin Orbital formalism consists of products of orbitals. The method can be used for any system, *sp* as well as narrow band ones. We demonstrate the applicability of our method by calculating the energy loss spectra of Ni, including local field effects which require the full dielectric matrix. Good agreement with experiment is found. The small number of basis functions makes the method suitable for self-energy calculations within the *GW* approximation, without making the so called plasmon pole approximation for the dielectric matrix.

I. Introduction

The response function of an electronic system has long been recognized as a basic quantity to describe many important properties of the system, such as optical, transport, electronic and magnetic properties. In this paper, we are concerned with the density-density response function, P, i.e. the function describing a change in the electron density $\delta\rho$ due to an external perturbation V^{ext}: $\delta\rho = \delta V^{ext} P$.

P is a basic ingredient in many-body perturbation theory, which has proven to be very successful in atomic physics [1]. Its application to electronic structures in solid-state physics, which is our main interest, has been very slow due to a prohibitively large computational size in obtaining P and also to a poor understanding of which perturbation series should be included. Even in the case of the electron gas, progress was made only recently and with a lot of effort [2, 3]. This is one of the reasons for resorting to model systems. Unfortunately, model calculations tell us little about the true magnitudes of quantities we are interested in. They are useful mainly to study mechanisms behind a physical phenomenon or to study trends. Their drawback lies in the use of adjustable parameters which, when not carefully chosen, can lead to misleading results.

Fortunately, *ab initio* many-body perturbation calculations have become feasible over the last few years, due to a rapid progress in the computer technology and a better understanding of the theory itself. With the invention of the linear method [4], we can now obtain single-particle bandstructures of complex systems with relative ease. They define the zeroth order Hamiltonian in a many-body perturbation calculation. A working approximation for the evaluation of a perturbation series was developed in the early sixties by Hedin, known as the GW approximation (GWA) [5, 6]. Formally, the GWA represents the first term in the expansion of the self-energy in the screened Coulomb potential W, but physically it is more illuminating to regard it as a generalization of the Hartree-Fock approximation. Unlike the Hartree-Fock theory, which has a long range exchange interaction that results in overestimated band gaps in insulators and total failure in metals, the GWA takes into account the screening of the Coulomb potential, remedying the most important flaw in the Hartree-Fock approximation. The GWA has been successful in describing quasiparticle properties in many systems [7, 8, 9, 10].

In most GW calculations, the screened potential $W = \epsilon^{-1}v$, where ϵ^{-1} is the screening matrix and v is the bare Coulomb potential, is calculated in a planewave basis. This is a very natural choice for systems that can be suitably treated with pseudopotentials [11] for two reasons: firstly, the single-particle wavefunctions, which are needed in the evaluation of P, are expanded in planewaves and secondly, the Coulomb potential becomes trivial since it is diagonalized by the planewaves. Other advantages of the planewave basis are a good control over convergence with respect to the number of basis functions and programming ease. There are, however, serious drawbacks:

1. It is not possible to do all-electron calculations. In many cases, it is important to include core electrons. For instance, in the case of Ni, the exchange of a valence state with the core states is $\sim -10\ eV$.

2. The number of planewaves becomes prohibitively large for narrow band systems.

Moreover, the planewaves have no direct physical interpretation, but this is a much less serious drawback.

To overcome these drawbacks, we simply abandon the pseudopotential method and planewave basis. The most efficient and physically transparent bandstructure method is the Linear Muffin Tin Orbital (LMTO) method, particularly within the so called Atomic Sphere Approximation (ASA) [4], where the Wigner-Seitz cells are replaced by overlapping spheres of equal volume. The LMTO method uses a minimal number of basis functions and we carry over the concept of the minimal basis in bandstructure to the dielectric matrix ϵ. Instead of a planewave basis, we use what we call a "product basis" which consists of products of LMTO's. As will be clear later, the product basis constitutes a minimal basis for ϵ within the LMTO formalism. A method for inverting the dielectric matrix using localized Wannier orbitals instead of planewaves has also been used in the context of local field and excitonic effects in the optical spectrum of covalent crystals [12].

Our method for evaluating ϵ can be used for any system, although our interest is in transition metals and their compounds (e.g. Ni and NiO). Due to a small number of basis functions, the method allows us to obtain the dielectric matrices for these systems without making the so called plasmon-pole approximation [13, 14, 15], whose validity in these systems is doubtful. We demonstrate the applicability of our method by calculating the energy loss spectra of Ni, including local field effects which require the full calculation of the dielectric matrix. We have also performed GW calculations for these narrow band systems, but this will be the subject of subsequent papers. In this paper we concentrate on the numerical machinery behind the calculations.

A different method for dealing with narrow band systems has also been devised before, using a modified Linear Augmented Plane Wave (LAPW) method for the bandstructure and basis functions [10, 16]. This method has been applied with success for calculating the energy loss spectra and self-energy of Ni. Due to a relatively large number of basis functions needed in the LAPW method, extension to larger systems is hampered by the computational size.

The paper is organized as follows: in section II we describe the theory and the method, in section III we apply the method to calculate the energy loss spectra of Ni. Finally, in section IV we draw our conclusions.

II. Theory

A. The Dielectric Matrix

The exact time ordered linear response function is given by [17]

$$P(1,2) = -i < 0|T[\tilde{\rho}(1)\tilde{\rho}(2)]|0> \tag{1}$$

where $1 \equiv (\mathbf{r}_1, t_1)$, $|0>$ is a many-body groundstate of an interacting system of N fermions, T is the Dyson time-ordering operator, and $\tilde{\rho}$ is the density fluctuation operator defined as

$$\tilde{\rho}(1) \equiv \rho(1) - < 0|\rho(1)|0> \tag{2}$$

with

$$\rho(1) \equiv \psi\dagger(1)\psi(1) \tag{3}$$

The field operator ψ is defined in the Heisenberg representation.

The response function P describes the change in the charge density $\delta\rho$ upon application of an external potential V^{ext}. This external potential is screened by the induced charge, and in the self-consistent Hartree approximation, the screened potential is the sum of the external field and the Coulomb field of the induced charge:

$$V^{scr} = V^{ext} + v\delta\rho \tag{4}$$

The change in the charge density may be expressed in two ways,

$$\begin{aligned} \delta\rho &= PV^{ext} \\ &= P^0 V^{scr} \end{aligned} \tag{5}$$

which defines P^0, often referred to as a polarization propagator. Substituting $\delta\rho$ into the previous equation yields

$$\begin{aligned} V^{scr} &= V^{ext} + v\delta\rho \\ &= [1 + vP]V^{ext} \\ &= [1 - vP^0]^{-1} V^{ext} \\ &= \epsilon^{-1} V^{ext} \end{aligned} \tag{6}$$

which defines the dielectric matrix ϵ and its inverse:

$$\epsilon = 1 - vP^0 \tag{7}$$

$$\epsilon^{-1} = 1 + vP \tag{8}$$

By multiplying ϵ and ϵ^{-1} it also follows that

$$\begin{aligned} P &= P^0 + P^0 v P \\ &= [1 - P^0 v]^{-1} P^0 \end{aligned} \tag{9}$$

In the Random Phase Approximation (RPA) [18], P^0 is approximated by a non-interacting response function described below. From Eq. (5), the physical interpretation of the RPA is that the electrons respond as non-interacting particles to the screened field (the sum of the perturbing field and the field from the induced charge).

The Lehmann (spectral) representation of P is given by

$$\begin{aligned} P(\mathbf{r}, \mathbf{r}'; \omega) = \sum_m & \left\{ \frac{< 0|\tilde{\rho}(\mathbf{r})|m >< m|\tilde{\rho}(\mathbf{r}')|0 >}{\omega - (E_m - E_0) + i\delta} \right. \\ & - \left. \frac{< 0|\tilde{\rho}(\mathbf{r}')|m >< m|\tilde{\rho}(\mathbf{r})|0 >}{\omega + (E_m - E_0) - i\delta} \right\} \end{aligned} \tag{10}$$

where $|m>$ and E_m are the m'th excited state and its energy respectively. For a non-interacting system P becomes

$$
\begin{aligned}
P^0(\mathbf{r},\mathbf{r}';\omega) &= \sum_{\mathbf{k}n}^{occ}\sum_{\mathbf{k}'n'}^{unocc} \psi^*_{\mathbf{k}n}(\mathbf{r})\psi_{\mathbf{k}'n'}(\mathbf{r})\psi^*_{\mathbf{k}'n'}(\mathbf{r}')\psi_{\mathbf{k}n}(\mathbf{r}') \\
&\times \left\{\frac{1}{\omega-(\epsilon_{\mathbf{k}'n'}-\epsilon_{\mathbf{k}n})+i\delta} - \frac{1}{\omega+(\epsilon_{\mathbf{k}'n'}-\epsilon_{\mathbf{k}n})-i\delta}\right\} \quad (11)
\end{aligned}
$$

where $\psi_{\mathbf{k}n}$ and $\epsilon_{\mathbf{k}n}$ are the Bloch state and its eigenenergy of the corresponding non-interacting Hamiltonian H^0. We have made use of the time-reversal symmetry in the above expression, i.e. for every $\psi_{\mathbf{k}n}$ there is $\psi^*_{-\mathbf{k}n}$ with the same eigenvalue. We may rewrite the above equation in terms of the non-interacting structure factor S^0 as follows (omitting space indices for clarity) [6]

$$
P^0(\omega) = \int_0^\infty d\omega' S^0(\omega')\left\{\frac{1}{\omega-\omega'+i\delta} - \frac{1}{\omega+\omega'-i\delta}\right\} \quad (12)
$$

with S^0 given by

$$
S^0(\mathbf{r},\mathbf{r}';\omega) = \sum_{\mathbf{k}n}^{occ}\sum_{\mathbf{k}'n'}^{unocc} \psi^*_{\mathbf{k}n}(\mathbf{r})\psi_{\mathbf{k}'n'}(\mathbf{r})\psi^*_{\mathbf{k}'n'}(\mathbf{r}')\psi_{\mathbf{k}n}(\mathbf{r}')\delta[\omega-(\epsilon_{\mathbf{k}'n'}-\epsilon_{\mathbf{k}n})] \quad (13)
$$

In full notation, the exact response function is approximated in RPA by the following integral equation:

$$
P(\mathbf{r},\mathbf{r}';\omega) = P^0(\mathbf{r},\mathbf{r}';\omega) + \int d^3r_1 d^3r_2 P^0(\mathbf{r},\mathbf{r}_1;\omega)v(|\mathbf{r}_1-\mathbf{r}_2|)P(\mathbf{r}_2,\mathbf{r}';\omega) \quad (14)
$$

The inverse dielectric matrix, which determines the screening, is given by

$$
\epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}') + \int d^3r'' v(|\mathbf{r}-\mathbf{r}''|)P(\mathbf{r}'',\mathbf{r}';\omega) \quad (15)
$$

Once we have obtained ϵ^{-1}, we can easily form the screened potential W, needed in the GW calculations:

$$
W(\mathbf{r},\mathbf{r}';\omega) = \int d^3r''\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)v(|\mathbf{r}''-\mathbf{r}'|) \quad (16)
$$

It is the computation of ϵ^{-1} that is the subject of the present paper.

To calculate ϵ^{-1} in real space is not feasible because $\mathbf{r}$ and $\mathbf{r}'$ are not restricted to a unit cell and ϵ^{-1} can be long range. The usual procedure is then to expand it in some basis. ϵ^{-1} may be expanded in any complete set of Bloch functions, $\{B_{\mathbf{k}i}\}$, in the following form

$$\epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega) = \sum_{\mathbf{k}}^{1stBZ} \sum_{ij} B_{\mathbf{k}i}(\mathbf{r})\epsilon_{ij}^{-1}(\mathbf{k},\omega)B_{\mathbf{k}j}^{*}(\mathbf{r}') \tag{17}$$

Due to the translational invariance of ϵ^{-1}

$$\epsilon^{-1}(\mathbf{r}+\mathbf{T},\mathbf{r}'+\mathbf{T};\omega) = \epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega) \tag{18}$$

where $\mathbf{T}$ is a translational vector, the expansion in Eq. (17) only involves a sum over one $\mathbf{k}$ variable, instead of two as in the general case. The coefficients of expansion are given by

$$\begin{aligned} \epsilon_{ij}^{-1}(\mathbf{k},\omega) &= < B_{\mathbf{k}i}|\epsilon^{-1}|B_{\mathbf{k}j} > \\ &= \int d^3r d^3r' B_{\mathbf{k}i}^{*}(\mathbf{r})\epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega)B_{\mathbf{k}j}(\mathbf{r}') \end{aligned} \tag{19}$$

assuming that $\{B_{\mathbf{k}i}\}$ are orthonormal. Similarly, P^0, P and v may also be expanded in the form above. To obtain ϵ^{-1}, we first calculate P^0 and the Coulomb potential v in a chosen basis. We then solve the matrix Eq. (14) to obtain P which gives ϵ^{-1}, with the use of Eq. (15).

In almost all calculations, the basis functions are chosen to be planewaves. As discussed in the Introduction, this choice is appropriate for systems that can be treated with pseudopotentials. Even for these *sp* systems, the computational size is still too large and one resorts to a plasmon-pole approximation. There are several versions of this approximation [13, 14], but the essence is to replace each matrix element of ϵ^{-1} by a delta function, whose position and weight are determined by the static and f-sum rules. A more general form has also been proposed recently [15]. The original idea of the plasmon-pole approximation goes back to Hedin [6] (p.84, Eq. (25.11)), in the context of the electron gas. In simple metals and *sp* semiconductors/insulators, the main plasmon excitation forms a well defined sharp peak, with little structure and well separated from the single-particle like excitations. The plasmon-pole approximation is expected to work well in these systems. In the heavy alkaline metal (Cs), however, the plasmon excitations already form several peaks [19]. Should one nevertheless try to use the plasmon-pole approximation by having several delta functions, instead of one delta function, to represent these peaks, one would run out of sum rules, needed to determine the positions and weights of these delta functions. In transition metals the situation is a lot worse because there are no well defined plasmon peaks in the first place [20, 16]. The plasmon and single-particle like excitations merge together, resulting in a complicated structure with two main peaks separated by a few eV, as can be seen in the energy loss spectra of Cu or Ni. For these systems, the plasmon-pole approximation is not expected to work well.

We would like to be able to treat not only *sp* systems, but also *d* and *f* systems with narrow bands without resorting to uncontrolled approximations such as the plasmon-pole approximation. Already with the former systems it is a large undertaking to calculate ϵ^{-1} without the plasmon-pole approximation, even when the systems are small. With the latter systems, we simply cannot afford to use planewaves and therefore we have taken a completely different approach which we describe below.

B. The Product Basis

Instead of using the pseudopotential method [11] to obtain the single-particle bandstructure $\{\psi_{\mathbf{k}n}, \epsilon_{\mathbf{k}n}\}$, we use the LMTO-ASA method [4], which allows us to treat virtually any system. The number of basis functions needed for an accurate description of the valence states is typically 9 (*spd*) or 16 (*spdf*). To calculate P^0, however, we need both the valence and conduction states, the latter can be up to $50 - 100$ eV, depending on the system. One expects that additional basis functions are needed for a proper description of the conduction bands. In a previous paper [21], we described how the LMTO method could be extended to handle both valence and high lying conduction states. The idea is to have multiple orbitals with different energies for a given $L \equiv lm$ channel.

In the LMTO-ASA method with multiple orbitals, the basis functions are of the form

$$\chi_{\mathbf{R}L\nu} = \phi_{\mathbf{R}L\nu} + \sum_{\mathbf{R}'L'\nu'} \dot{\phi}_{\mathbf{R}'L'\nu'} h_{\mathbf{R}'L'\nu',\mathbf{R}L\nu} \tag{20}$$

where $L\nu$ denote the angular momentum and principal quantum number, $\phi_{\mathbf{R}L\nu}$ is a radial solution to the Schrödinger equation inside a sphere centered on an atom at site $\mathbf{R}$ for a certain energy ϵ_ν, normally chosen at the center of the band, and $\dot{\phi}$ is the energy derivative of ϕ at ϵ_ν. An important point to note is that both ϕ and $\dot{\phi}$ are *independent* of $\mathbf{k}$ and band index

n. Information about the lattice structure and the scattering phase shifts (logarithmic derivatives of the wavefunctions at the surface of the Wigner-Seitz spheres) is carried in h, which therefore contains the $\mathbf{k}$ dependence when a Bloch sum is performed. For more details we refer to [21]. The wavefunctions are expanded in these LMTO's

$$\psi_{\mathbf{k}n} = \sum_{\mathbf{R}L\nu} \chi_{\mathbf{R}L\nu}(\mathbf{k}) b_{\mathbf{R}L\nu}(\mathbf{k}n) \tag{21}$$

Unlike the pseudopotential method with a planewave basis, it is not clear anymore what basis functions should now be used to expand ϵ^{-1}. Let us introduce a notation:

$$\{P^0\} \equiv Hilbert\ space\ spanned\ by\ P^0 \tag{22}$$

To solve the problem, we first figure out what Hilbert space is spanned by ϵ^{-1}. We expand Eq. (14)

$$P = P^0 + P^0 v P^0 + P^0 v P^0 v P^0 + \ldots \tag{23}$$

Since v is always sandwiched between two P^0's, it is clear that $\{P\}$, is identical to $\{P^0\}$ and to obtain P we must work in $\{P^0\}$. Thus, from Eq. (15) we see that $\{\epsilon^{-1}\}$ is the union between $\{P^0\}$ and $\{v\}$,

$$\{\epsilon^{-1}\} = \{P^0\} \cup \{v\} \tag{24}$$

In practice, however, we usually take matrix elements of ϵ^{-1}, or use it in conjunction with other quantities so that we may not actually need the entire space. We consider two examples which are closely related to our interest.

1) The energy loss spectra which is given by

$$\begin{aligned} \epsilon^{-1}(\mathbf{q},\omega) &= <\mathbf{q}|\epsilon^{-1}(\omega)|\mathbf{q}> \\ &= 1 + <\mathbf{q}|vP^0|\mathbf{q}> + <\mathbf{q}|vP^0vP^0|\mathbf{q}> + \ldots \\ &= 1 + v(\mathbf{q})\{<\mathbf{q}|P^0|\mathbf{q}> + <\mathbf{q}|P^0vP^0|\mathbf{q}> + \ldots\} \end{aligned} \tag{25}$$

where $|\mathbf{q}>= 1/\sqrt{V} exp(i\mathbf{q}\cdot\mathbf{r})$ and $v(\mathbf{q}) = 4\pi/q^2$. We can read off from the above equations that the required Hilbert space is

$$\{\epsilon^{-1}(\mathbf{q},\omega)\} = \{P^0\} \tag{26}$$

2) The self-energy of a given state $\psi_{\mathbf{k}n}$ in the GWA has the form [10]

$$\begin{aligned}\Sigma(\mathbf{k}n,\omega) &= <\psi_{\mathbf{k}n}|GW|\psi_{\mathbf{k}n}> \\ &= <\psi_{\mathbf{k}n}\psi|v|\psi\psi_{\mathbf{k}n}> + <\psi_{\mathbf{k}n}\psi|vPv|\psi\psi_{\mathbf{k}n}>\end{aligned} \tag{27}$$

We have written the above equation in a very schematic form without summations and indices in order to bring out the main point. The extra ψ comes from the Green function G which consists of all states (core,valence and conduction),

$$\{\psi\} \equiv \{\psi_{core}\} + \{\psi_{val}\} + \{\psi_{cond}\} \tag{28}$$

The first term in 27 is the bare exchange and the second term is the correlated part. Again we can read off from the above equations, what Hilbert space we need. For the exchange term, the required Hilbert space is

$$\{\Sigma^x\} = \{\psi_{\mathbf{k}n}(\psi_{core} + \psi_{val})\} \tag{29}$$

since the exchange part only involves summation over occupied states. In principle we need only the overlap between the above space and $\{v\}$, but it is unlikely that there exists a function $f \in \{\Sigma^x\}$, such that $< f|v|f >= 0$. For the correlated part the Hilbert space is

$$\{\Sigma^c\} = \{\psi_{\mathbf{k}n}\psi\} \cup \{P^0\} \tag{30}$$

which also covers $\{\Sigma^x\}$. $\{v\}$ alone is also possible, but this is probably more than necessary.

Since it is unlikely that one can construct a small but complete basis for expanding $v = 1/|\mathbf{r} - \mathbf{r}'|$ in a separable form like in Eq. (17), we proceed by considering the space in Eq. (30). From Eq. (26), this space is also sufficient to describe the energy loss spectra. From Eq. (11) we have

$$\begin{aligned}\{P^0\} &= \{\psi^{occ}\psi^{unocc}\} \\ &= \{\psi_{core}\psi_{cond}\} + \{\psi_{val}\psi_{cond}\}\end{aligned} \tag{31}$$

The first term is only necessary when core polarization is important. In GW calculations, one is usually interested in the valence states and a few of the low lying conduction states. Let us assume that $\{\psi_{\mathbf{k}n}\} = \{\psi_{val}\}$, keeping in mind that it might include some conduction states. Then from Eqs. (30) and (31), the total Hilbert space required is

$$\{\Sigma\} = \{(\psi_{core} + \psi_{val})(\psi_{val} + \psi_{cond})\} \tag{32}$$

$\{\psi_{core}\}$ may be neglected when core polarization is not important.

For practical purpose, the above equation is not very useful because $\{\psi\}$ depends on $\mathbf{k}$. In the LMTO method, however, the basis functions consist of ϕ and $\dot{\phi}$ which are $\mathbf{k}$ independent. Schematically, from Eq. (21), we have

$$\begin{aligned} \psi\psi &= (\chi b)(\chi b) \\ &= (\phi + \dot{\phi}h)(\phi + \dot{\phi}h)b^2 \\ &= [\phi\phi + (\phi\dot{\phi} + \dot{\phi}\phi)h + \dot{\phi}\dot{\phi}h^2]b^2 \end{aligned} \tag{33}$$

This equation displays very clearly the Hilbert space spanned by $\{\Sigma\}$. Since h and b are just matrices, we may rewrite Eq. (32) as

$$\{\Sigma\} = \{\phi\phi\} + \{\phi\dot{\phi}\} + \{\dot{\phi}\dot{\phi}\} \tag{34}$$

If we include all the possible products of $\phi\phi$, $\phi\dot{\phi}$ and $\dot{\phi}\dot{\phi}$, then we have a complete basis *by construction*. By performing a Gramm-Schmidt orthogonalization, we end up with a set of orthonormal basis functions, which must be the smallest we can have within the LMTO formalism. The number of products in Eq. (34) can still be large. With 9 *spd* orbitals, excluding core states, the total number of product functions is $3 \times 9 \times (9+1)/2 = 135$. With 16 *spdf* orbitals we have $3 \times 16 \times (16+1)/2 = 408$.

We reduce the number of product functions in three steps:

1) We note that in practice, the magnitude of $\dot{\phi}$ is small, typically 10% of ϕ and therefore to a good approximation the last two terms in Eq. (34) may be negelected, which reduces the number of product functions by a factor of 3.

2) In Eq. (32), there are no products between conduction states. Normally in *sp* and d systems, the d and respectively f orbitals, have most of their weight in the conduction states and therefore products of $\phi_d\phi_d$ and $\phi_f\phi_f$ may be neglected in *sp* and d systems respectively.

3) The remaining product functions turn out to have a large number of linear dependencies, typically $30 - 50\%$. We sort out these linear dependencies in a systematic way, by calculating the eigenvalues and eigenvectors of the overlap matrix of the product functions, and throw away those eigenvectors with eigenvalues smaller than some tolerance ($<\sim 10^{-4}$). The resulting orthonormal functions are linear combinations of the product functions, and typically $\sim 70 - 100$ per atom with *spdf* orbitals.

Let us now give a proper definition of the product basis. In general, a product function is defined by

$$\tilde{B}_i(\mathbf{r}) \equiv \chi_{\mathbf{R}L\nu}(\mathbf{r})\chi_{\mathbf{R}'L'\nu'}(\mathbf{r}) \; ; \; i = (\mathbf{R}L\nu, \mathbf{R}'L'\nu') \tag{35}$$

With the simplification 1) the product function becomes

$$\tilde{B}_i(\mathbf{r}) \equiv \phi_{\mathbf{R}L\nu}(\mathbf{r})\phi_{\mathbf{R}L'\nu'}(\mathbf{r}) = \phi_{\mathbf{R}l\nu}(r)\phi_{\mathbf{R}l'\nu'}(r)y_L(\hat{\mathbf{r}})y_{L'}(\hat{\mathbf{r}}) \tag{36}$$

where $i = (\mathbf{R}, L\nu, L'\nu')$. This function is only non-zero inside a sphere centered on atom $\mathbf{R}$. Thus, there are no products between orbitals centered on different spheres. For a periodic system we need a Bloch basis and perform a Bloch sum

$$\tilde{B}_{\mathbf{k}i}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}}\phi_{\mathbf{R}L\nu}(\mathbf{r}-\mathbf{R}-\mathbf{T})\phi_{\mathbf{R}L'\nu'}(\mathbf{r}-\mathbf{R}-\mathbf{T}) \tag{37}$$

The $\mathbf{k}$ dependence is in some sense artificial because the function has no overlap with neighbouring spheres, similar to core states. After leaving out unnecessary products (step 2), we optimize the basis by sorting out linear dependencies (step 3). This is done by orthogonalizing the overlap matrix

$$O_{ij} =< \tilde{B}_i|\tilde{B}_j > \tag{38}$$

$$Oz = ez \tag{39}$$

and throwing away eigenvectors z_i with eigenvalues ϵ_i < tolerance. The resulting optimal product basis is given by

$$B_i = \sum_j \tilde{B}_j z_{ji} \tag{40}$$

This basis is orthonormal.

To check the completeness of our basis, we perform the following test for Ni. We take a product of two wavefunctions and expand it in the optimal product basis

$$\psi^*_{\mathbf{k}n}\psi_{\mathbf{k}'n'} = \sum_i B_i c_i \tag{41}$$

For a complete basis we have

$$\sum_i |c_i|^2 = | < \psi_{\mathbf{k}n}|\psi_{\mathbf{k}'n'} > |^2 \tag{42}$$

In Table 1 we show the result of this test. The basis is practically complete except for the last few high lying conduction states. This is because $\dot{\phi}$, which have been neglected in the product basis, become more important for the broad high lying conduction states. Also, the optimization procedure puts less weight on those products which have smaller overlap. This is not crucial for two reasons: the matrix elements become smaller for the higher states, and in relation to GW calculations, there is a factor of $1/\omega$ which makes the higher states less important.

II. Applications:
Electron Energy Loss Spectra of Ni

The Electron Energy Loss Spectra (EELS) measures the energy loss suffered by fast electrons when going through a solid by creating single-particle like excitations and collective excitations, mainly plasmons. It is given by the imaginary part of the inverse dielectric function [18]

$$\begin{aligned} EELS &= Im\, \epsilon^{-1}(\mathbf{q},\omega) \\ &= Im\, \frac{1}{V}\int d^3r d^3r' e^{-i\mathbf{q}\cdot\mathbf{r}} \epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega) e^{i\mathbf{q}\cdot\mathbf{r}'} \end{aligned} \tag{43}$$

In most calculations, $\epsilon^{-1}(\mathbf{q},\omega)$ is approximated by $1/\epsilon(\mathbf{q},\omega)$, which corresponds to neglecting the local field arising from the nonhomogeneity of the charge density. By $\epsilon(\mathbf{q},\omega)$ we mean the Fourier transform of $\epsilon(\mathbf{r},\mathbf{r}';\omega)$, like in Eq. (43). The approximation becomes exact when the charge density is homogeneous. A number of calculations have included the local field effects in semiconductors [22, 23, 15]. However, only one calculation for a transition metal (Ni) [16] has been performed so far. Most recently, local field effects have also been considered in the calculations of plasmon dispersions in light alkali metals [24] and heavy alkali metals [19].

We consider explicitly what we mean by local field effects by considering the screening of an external field

$$V^{ext}(\mathbf{r},t) = V^{ext}(\mathbf{q},\omega)e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)} \tag{44}$$

From Eq. (5), the Fourier component of the induced charge in RPA is

$$\begin{aligned} \delta\rho(\mathbf{q},\omega) &= <\mathbf{q}|P^0 V^{scr}|\mathbf{q}> \\ &= \sum_i <\mathbf{q}|P^0|i><i|V^{scr}|\mathbf{q}> \\ &= P^0(\mathbf{q},\omega)V^{scr}(\mathbf{q},\omega) + \sum_{i\neq\mathbf{q}} <\mathbf{q}|P^0|i><i|V^{scr}|\mathbf{q}> \end{aligned} \tag{45}$$

where $\{|i>\} = \{P^0\}$, a set of states that spans the space of P^0. The first term represents the induced charge without local field, which neglects the inhomogeneity of the screened potential represented by the second term. From Eqs. (5) and (6), the Fourier component of the screened potential is given by

$$\begin{aligned} V^{scr}(\mathbf{q},\omega) &= V^{ext}(\mathbf{q},\omega) + v(\mathbf{q})P^0(\mathbf{q},\omega)V^{scr}(\mathbf{q},\omega) \\ &+ v(\mathbf{q})\sum_{i\neq\mathbf{q}} <\mathbf{q}|P^0|i><i|V^{scr}|\mathbf{q}> \end{aligned} \tag{46}$$

The last term is the local field correction to the screened potential. Without local field, V^{scr} reduces to

$$\begin{aligned} V^{scr}(\mathbf{q},\omega) &= V^{ext}(\mathbf{q},\omega) + v(\mathbf{q})P^0(\mathbf{q},\omega)V^{scr}(\mathbf{q},\omega) \\ &= \frac{V^{ext}(\mathbf{q},\omega)}{1 - v(\mathbf{q})P^0(\mathbf{q},\omega)} \end{aligned} \tag{47}$$

$\epsilon^{-1}(\mathbf{q},\omega)$ is defined as

$$\epsilon^{-1}(\mathbf{q},\omega) \equiv \frac{V^{scr}(\mathbf{q},\omega)}{V^{ext}(\mathbf{q},\omega)} \tag{48}$$

Thus, without local field effects we have

$$\begin{aligned} \epsilon^{-1}(\mathbf{q},\omega) &= 1/[1 - v(\mathbf{q})P^0(\mathbf{q},\omega)] \\ &= 1/\epsilon(\mathbf{q},\omega) \end{aligned} \tag{49}$$

and the local field correction is given by

$$\begin{aligned} LF &= v(\mathbf{q})\sum_{i\neq\mathbf{q}} <\mathbf{q}|P^0|i><i|V^{scr}|\mathbf{q}> /V^{ext}(\mathbf{q},\omega) \\ &= v(\mathbf{q})\sum_{i\neq\mathbf{q}} <\mathbf{q}|P^0|i><i|V^{ext} + vPV^{ext}|\mathbf{q}> /V^{ext}(\mathbf{q},\omega) \\ &= v(\mathbf{q})\sum_{i,j\neq\mathbf{q}} <\mathbf{q}|P^0|i><i|v|j><j|P|\mathbf{q}> \end{aligned} \tag{50}$$

keeping in mind that v is diagonalized by the planewaves and V^{ext} does not have higher Fourier components.

To calculate ϵ^{-1} we first calculate P^0 in the product basis:

$$\begin{aligned} P^0_{ij}(\mathbf{q},\omega) &= \sum_{\mathbf{k}}\sum_{n}^{occ}\sum_{n'}^{unocc} <B_{\mathbf{q}i}\psi_{\mathbf{k}n}|\psi_{\mathbf{k+q}n'}><\psi_{\mathbf{k+q}n'}|\psi_{\mathbf{k}n}B_{\mathbf{q}j}> \\ &\times \left\{\frac{1}{\omega - \epsilon_{\mathbf{k+q}n'} + \epsilon_{\mathbf{k}n} + i\delta} - \frac{1}{\omega + \epsilon_{\mathbf{k+q}n'} - \epsilon_{\mathbf{k}n} - i\delta}\right\} \end{aligned} \tag{51}$$

We must also calculate the Coulomb potential v in the product basis, which is described in Appendix A. We then use Eqs. (8) and (9) to obtain P and ϵ^{-1}.

To calculate the energy loss spectra, however, it is more efficient to calculate S^0 in Eq. (13):

$$S^0_{ij}(\mathbf{q},\omega) = \sum_{\mathbf{k}}\sum_{n}^{occ}\sum_{n'}^{unocc} < B_{\mathbf{q}i}\psi_{\mathbf{k}n}|\psi_{\mathbf{k+q}n'} >< \psi_{\mathbf{k+q}n'}|\psi_{\mathbf{k}n}B_{\mathbf{q}j} > \times \delta(\omega - \epsilon_{\mathbf{k+q}n'} + \epsilon_{\mathbf{k}n}) \tag{52}$$

and use the Kramers-Kronig relation in Eq. (12), than to calculate P^0 directly. In the actual calculations, the delta function is replaced by a Gaussian

$$\delta(\omega) \rightarrow \frac{1}{\sigma\sqrt{\pi}} e^{-\omega^2/\sigma^2} \tag{53}$$

with $\sigma = 0.2\ Ry$. The energy loss spectra including local field is given by

$$Im\ \epsilon^{-1}(\mathbf{q},\omega) = Im \sum_{ij} < \mathbf{q}|B_{\mathbf{q}i} > \epsilon^{-1}_{ij}(\mathbf{q},\omega) < B_{\mathbf{q}j}|\mathbf{q} > \tag{54}$$

where $< \mathbf{q}|B_{\mathbf{q}i} >$ is the Fourier transform of the product basis and $\epsilon^{-1}_{ij}(\mathbf{q},\omega)$ is the matrix element of ϵ^{-1} in the product basis.

We have made a systematic study of Ni energy loss spectra, concerning the importance of high lying states and the sensitivity with respect to the quality of the transition matrix elements. This study can be carried out within the LMTO formalism in a very natural way. Our starting Hamiltonian for the evaluation of P^0 is the Local Density Hamiltonian [25]:

$$H^0 = T + V_H + V_{xc} \tag{55}$$

and the dielectric matrix has been obtained within the RPA. We have calculated all spectra with and without local field for $\mathbf{q} = (.25\ 0\ 0)2\pi/a$, $a = 6.654\ a_0$.

We start with the energy loss spectra obtained with only *spd* orbitals in the LMTO basis. The result is shown in Fig. 1. The neglect of f orbitals centered at $\sim 50\ eV$ is reflected in the absence of intensity between 40 to 60 eV. The $3p$ core excitations starting at 67 eV is not affected by the neglect of the f orbitals since they are transitions to the unoccupied states above the Fermi level. It is interesting to note that although the f-sum rule is off by almost a factor of two, the static sum rule is given correctly. The large peak at 27 eV compensates the lack of intensity in the energy region above it. We have no proof that this is a general result, but we do not think that it is a mere coincidence. It has an important implication in the GW calculations because the self-energy is given by an integral of the form $\int d\omega' W(\omega + \omega')/\omega'$.

We concentrate first on improving the bandstructure by enlarging the LMTO basis functions, including more orbitals one at a time. We now include the f orbitals and show the resulting energy loss spectra in Fig. 1. A marked improvement is obtained, which is not surprising because d to f transitions must be significant. The discrepancy between the calculated and experimental spectra is still quite large. The position of the second main peak is to high by 6 eV and the intensity above 40 eV is too large, particularly at the onset of the $3p$ core excitations.

To improve the bandstructure further, we include the g orbitals and the resulting energy loss spectra are shown in Fig. 1. An improvement is obtained in the high energy region above 60 eV which is to be expected, but the rest of the discrepancies still remain. These discrepancies suggest that we have not obtained the right bandstructure and the transition matrix elements are not accurately calculated. Indeed we have shown in a previous paper that $spdf$ or even $spdfg$ orbitals are not sufficient for a proper description of the high lying conduction states. Inclusion of the second d orbitals i.e. $4d$ orbitals, in the basis functions is crucial and they were found to change the bandstructure above 30 eV dramatically.

In Fig. 2 we show the effects of adding the $4d$ orbitals to the LMTO basis. The main improvements are the shifting of the second main peak by 3 eV to lower energy and the reduction in intensity in the region between 40 and 60 eV. The large peak at the onset of the $3p$ core excitations is shifted to higher energy, but the magnitude is still too large.

We have exhausted all possible orbitals we can have. Addition of h orbitals are not expected to have significant effects since their energies are very high. We have also performed calculations with the addition of the second s and p orbitals and found almost no improvement.

We now attempt to improve the quality of the transition matrix elements. The separation between the effects of bandstructure and matrix elements is certainly not clear cut, because improving the bandstructure implies better wavefunctions which in turn means improved matrix elements. However, by improving the matrix elements we mean that we correct or reduce the dependence on the ASA. One way of doing this is to add empty spheres. This procedure does not completely eliminate the ASA, but it should give an improvement. One might think that for a close packed structure like Ni, it is unlikely that empty spheres would have any significance. This is true for the valence states, but for the high lying conduction states, we found a significant effect.

In Fig. 3 we show the spectra, calculated with the addition of an empty sphere located at $(.5\ .5\ .5)a$. A good agreement with experiment is obtained, in particular the positions of the two main peaks are very close to the experimental peaks, with a 1 eV shift to higher energy. The magnitude is somewhat too large, but we would like to point out that it is sensitive to the choice of broadening used in the calculations, as may be seen in Fig. 4 where the spectra are calculated with $\sigma = 0.1\ Ry$ and $\sigma = 0.2\ Ry$. Increasing the broadening will reduce the heights of the peaks further, but the structure in the rest of the spectra is lost.

In our calculations, we have found that the local field effects are small, except for energies above 50 eV, as may be seen in Fig. 5. This result is surprising because the charge density in Ni is very far from homogeneous and one expects that the corresponding screened potential would be highly inhomogeneous resulting in a large local field correction given in Eq. (50). Since P^0 itself must have high Fourier components, the result suggests that the screened potential does not have significantly high Fourier components. Since the objective of this paper is to describe the method of calculating dielectric matrices, we present a detailed investigation of the local field effects in a forthcoming paper [26].

We compare in Fig. 6 our present results with a previous work which used a modified LAPW method for the bandstructure and the basis functions. The second main peak in the previous calculation is somewhat larger than the present one, but on the other hand the intensity at high energies is better described than in the present calculations. As shown in Fig. 4, the magnitude of the peaks can be sensitive to the choice of broadening. The agreement is nevertheless satisfactory considering that the two methods are very different.

To show that our method also works for *sp* systems, we have calculated the energy loss spectra of Si which have been the subject of several investigations [22, 23, 15]. The result is shown in Fig. 7. A large reduction in the magnitude of the plasmon peak due to local field effects is observed, which has also been reported elsewhere. The calculated spectra correspond to $\mathbf{k} = (.25\ 0\ 0)2\pi/a = .3\ \mathring{A}^{-1}$, which is larger than the wavevector in the experiment ($.067\ \mathring{A}^{-1}$). This explains the smaller magnitude of the calculated plasmon peak which results in a larger width. Another interesting feature is the splitting of the plasmon peak, as also found by Engel [15], whose origin may be assigned to local field effects. However, the separation between the two peaks is quite large (2.5 eV), significantly larger than the experimental resolution ($\sim .8$ eV), and therefore it is not likely that the experiment has missed this splitting, unless there are other broadening effects such as those due to impurities. We would like to point out that the peak structure can be very sensitive to the quality of the wavefunctions.

IV. Summary and Conclusions

We have developed a method for calculating the dielectric matrix of a periodic system using a product basis. The method is applicable to any system, sp as well as narrow band systems, as the examples on energy loss spectra have shown. Our method has several advantages over methods based on planewaves. The main advantages are: a small number of basis functions, core polarization can be easily incorporated and there is no restriction to any particular system. In the Ni case for instance, there is no difficuly in including all the core states and the computational effort is about the same as for Si. This is not the case in methods based on a planewave basis. A very large number of planewaves would be needed to describe the rather localized d states, not to mention the core states, which makes the computation very expensive, if at all possible.

The relatively small number of basis functions allows us to perform GW calculations without making a plasmon pole approximation. Nevertheless, it is still very demanding computationally and an efficient way of calculating P^0 is needed without making too much sacrifice on the accuracy. It is one of the objectives of the present work to find such an efficient scheme, but in order to have a controlled scheme, one must be able to do the full calculations for the purpose of comparison.

As applications of the method we have calculated the energy loss spectra of Ni and Si. A good agreement with experimental results is found in both cases. We have done a systematic study regarding the importance of high lying states and the quality of the transition matrix elements in Ni. It was found that inclusion of the $4d$ orbitals is important for a good description of the energy loss spectra. This is consistent with the bandstructure calculations described in a previous work [21], where it was found that the $4d$ orbitals dramatically changed the bandstructure above 30 eV.

We have performed all the calculations with and without local field effects. The origin of local field effects is an interesting subject, but has not been studied in detail so far. In our calculations, the local field effects in Ni were found to be small, except at energies above 50 eV. In Si on the other hand, the local field effects are large. In a forthcoming paper [26], we investigate in detail the origin of the local field effects and offer an explanation, why the local field effects in Ni are small whereas in Si they are large.

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Appendix A

Evaluation of the Coulomb Matrix

We consider one atom per unit cell for simplicity. Extension to several atoms is straightforward. The Coulomb matrix is given by

$$v_{ij}(\mathbf{q}) = \int d^3r \int d^3r' \frac{B^*_{\mathbf{q}i}(\mathbf{r}) B_{\mathbf{q}j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{56}$$

The integrations over the whole space may be reduced to integrations over a unit cell Ω by using the property

$$B_{\mathbf{q}i}(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{q}\cdot\mathbf{T}} B_{\mathbf{q}i}(\mathbf{r}) \tag{57}$$

and noting that the integration over $\mathbf{r}'$ is independent of the origin of $\mathbf{r}$. This gives

$$v_{ij}(\mathbf{q}) = \int_\Omega d^3r \int_\Omega d^3s B^*_{\mathbf{q}i}(\mathbf{s}) E_{\mathbf{q}}(\mathbf{s},\mathbf{r}) B_{\mathbf{q}j}(\mathbf{r}) \tag{58}$$

where

$$E_{\mathbf{q}}(\mathbf{s},\mathbf{r}) = \sum_{\mathbf{T}} \frac{e^{i\mathbf{q}\cdot\mathbf{T}}}{|\mathbf{s}-\mathbf{r}-\mathbf{T}|}$$

$$
\begin{aligned}
&= \frac{4\pi}{\Omega}\sum_{\mathbf{G}} \frac{e^{-(\mathbf{q}+\mathbf{G})^2/4\alpha^2}}{(\mathbf{q}+\mathbf{G})^2} e^{i(\mathbf{q}+\mathbf{G})\cdot(\mathbf{s}-\mathbf{r})} \\
&+ \alpha \sum_{\mathbf{T}} e^{i\mathbf{q}\cdot\mathbf{T}} \frac{erfc(\alpha|\mathbf{s}-\mathbf{r}-\mathbf{T}|)}{\alpha|\mathbf{s}-\mathbf{r}-\mathbf{T}|}
\end{aligned} \tag{59}
$$

The Ewald method has been used to obtain the above decomposition into summations in the reciprocal and real space. $erfc$ is the complementary error function equal to $(1 - erf)$, and α is an arbitrary constant whose value is chosen to give a fast convergence in the number of reciprocal lattice vectors and the number of neighbours. The essence of the Ewald method is to add and substract a Gaussian charge distribution which breaks the Coulomb potential from a point charge into a short and long range part. The short range part is done in real space and the long range part is done in reciprocal space. The main task is to calculate the potential

$$
P_{\mathbf{q}j}(\mathbf{s}) = \sum_i \tilde{P}_{\mathbf{q}i}(\mathbf{s}) z_{ij} \tag{60}
$$

with z given by Eq. (40) and

$$
\begin{aligned}
\tilde{P}_{\mathbf{q}i}(\mathbf{s}) &= \int_\Omega d^3r \tilde{B}_{\mathbf{q}i}(\mathbf{r}) E_{\mathbf{q}}(\mathbf{s},\mathbf{r}) \\
&= \sum_{\mathbf{G}} \tilde{P}_{\mathbf{q}i}(\mathbf{s},\mathbf{G}) + \sum_{\mathbf{T}} \tilde{P}_{\mathbf{q}i}(\mathbf{s},\mathbf{T})
\end{aligned} \tag{61}
$$

where

$$
\tilde{P}_{\mathbf{q}i}(\mathbf{s},\mathbf{G}) = \frac{4\pi}{\Omega} \frac{e^{-(\mathbf{q}+\mathbf{G})^2/4\alpha^2}}{(\mathbf{q}+\mathbf{G})^2} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{s}} \int_\Omega d^3r e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \tilde{B}_{\mathbf{q}i}(\mathbf{r}) \tag{62}
$$

and

$$
\tilde{P}_{\mathbf{q}i}(\mathbf{s},\mathbf{T}) = \alpha e^{i\mathbf{q}\cdot\mathbf{T}} \int_\Omega d^3r \frac{erfc(\alpha|\mathbf{s}-\mathbf{r}-\mathbf{T}|)}{\alpha|\mathbf{s}-\mathbf{r}-\mathbf{T}|} \tilde{B}_{\mathbf{q}i}(\mathbf{r}) \tag{63}
$$

It is straightforward to calculate $\tilde{P}_{\mathbf{q}j}(\mathbf{s},\mathbf{G})$, since it is a Fourier transform of $\tilde{B}_{\mathbf{q}j}(\mathbf{r})$. To calculate $\tilde{P}_{\mathbf{q}i}(\mathbf{s},\mathbf{T})$, we use the following expansion formulas

$$
\frac{1}{|\mathbf{s}-\mathbf{r}|} = \sum_L \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} y_L(\hat{\mathbf{s}}) y_L(\hat{\mathbf{r}}) \tag{64}
$$

and

$$
\frac{erf(\alpha|\mathbf{s}-\mathbf{r}|)}{\alpha|\mathbf{s}-\mathbf{r}|} = \sum_L \frac{4\pi}{2l+1} g_l(r,s) y_L(\hat{\mathbf{s}}) y_L(\hat{\mathbf{r}}) \tag{65}
$$

The coefficients $g_l(r,s)$ are determined by numerical integrations using special directions [16].

At the central sphere, $\tilde{B}_{\mathbf{q}i}(\mathbf{r})$ has no $\mathbf{q}$ dependence and is given by Eq. (36), so that

$$\tilde{P}_{\mathbf{q}i}(\mathbf{s},\mathbf{T}) = \alpha e^{i\mathbf{q}\cdot\mathbf{T}} \sum_L w_{li}(s_{\mathbf{T}}) y_L(\hat{\mathbf{s_T}}) \int d\Omega y_{L_1} y_{L_2} y_L \tag{66}$$

where $\mathbf{s_T} = \mathbf{s} - \mathbf{T}$ and

$$w_{li}(s_{\mathbf{T}}) = \frac{4\pi}{2l+1} \int_0^R dr r^2 \left\{ \frac{r_<^l}{r_>^{l+1}} - g_l(r, s_{\mathbf{T}}) \right\} \tilde{B}_i(r) \tag{67}$$

We note that the sum over L is cut off by L_1 and L_2 in the product function $\tilde{B}$. The final integration over $\mathbf{s}$ is easily done with special directions [16].

TABLE 1. The completeness test of the optimal product basis for Nickel. A product of two wavefunctions is expanded in the basis: $\psi^*_{\mathbf{k}n}\psi_{\mathbf{k}'n'} = \sum_i B_i c_i$ with $\mathbf{k} = (0\ 0\ 0)$, $\epsilon_{\mathbf{k}n} = -1.22\ eV$ (the higest valence state at the Γ point) and $\mathbf{k}' = (.5\ .5\ .5)$. The basis is complete if $|\sum_i |c_i|^2 = |<\psi_{\mathbf{k}n}|\psi_{\mathbf{k}'n'}>|^2$. The number of optimal product basis functions is 101 and 82 with and without $3s, 3p$ core states respectively.

$Core$	$\|<\psi_{\mathbf{k}n}\|\psi_{core}>\|^2$	$\sum_i \|c_i\|^2$	error
3s	.158114	.158113	.000001
3p	.066833	.066832	.000001
3p	.209174	.209172	.000002
3p	.168184	.168183	.000001

$\epsilon_{\mathbf{k}'n'}(eV)$	$\vert < \psi_{\mathbf{k}n} \vert \psi_{\mathbf{k}'n'} > \vert^2$	$\sum_i \vert c_i \vert^2$	error
-9.09	.052222	.052220	.000002
-2.23	.181724	.181722	.000002
-2.23	.101124	.101124	.000000
-2.23	.167753	.167743	.000010
-1.22	.119586	.119583	.000003
-1.22	.014565	.014537	.000028
24.39	.060638	.060634	.000004
28.19	.013188	.013074	.000114
28.19	.008852	.008736	.000116
28.19	.001883	.001738	.000145
42.29	.015563	.015400	.000163
42.29	.018353	.018167	.000186
42.29	.006292	.006040	.000252
73.89	.017300	.016660	.000640
73.89	.011847	.011409	.000438
73.89	.013877	.012911	.000966

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Figure 1

Loss spectra of ferromagnetic Ni obtained with increasing number of LMTO basis: with $4s$, $4p$, $3d$ orbitals (dash-dotted line), $4s$, $4p$, $3d$, $4f$ orbitals (dotted line) $4s$, $4p$, $3d$, $4f$, $5g$ orbitals (solid line). All cases include core excitations. The solid circles are the experimental result.

Figure 2

The effect of including the $4d$ orbitals on the loss spectra of Ni. The dotted line with $4s$, $4p$, $3d$, $4f$, $5g$ orbitals and the solid line with $4s$, $4p$, $3d$, $4d$, $4f$, $5g$ orbitals. Both cases include core excitations. The solid circles are the experimental result.

Figure 3

The effect of including an empty sphere on the loss spectra of Ni. The empty sphere is located at $(.5\ .5\ .5)a$. The solid and dotted lines are the loss spectra obtained with and without an empty sphere respectively. Both spectra are calculated with $4s$, $4p$, $3d$, $4d$, $4f$, $5g$ orbitals including core excitations. The solid circles are the experimental result.

Figure 4

The effect of Gaussian broadening on the loss spectra of Ni. The solid and dotted lines are the loss spectra obtained with $\sigma = 0.2\ Ry$ and $\sigma = 0.1\ Ry$ respectively. Both spectra are calculated with $4s$, $4p$, $3d$, $4d$, $4f$, $5g$ orbitals including an empty sphere at $(.5\ .5\ .5)a$ and core excitations. The Gaussian broadening $\sigma = 0.2\ Ry$.

Figure 5

The effect of local field on the loss spectra of Ni. The solid and dotted lines are the loss spectra with and without local field corrections respectively.

Both spectra are calculated with $4s$, $4p$, $3d$, $4d$, $4f$, $5g$ orbitals including an empty sphere at $(.5\ .5\ .5)a$ and core excitations.

Figure 6

Comparison between the loss spectra of Ni obtained with a modified LAPW method [16] (dotted line) and the present method (solid line). Both spectra are calculated with $\sigma = 0.1\ Ry$ and the solid curve is calculated with $4s$, $4p$, $3d$, $4d$, $4f$, $5g$ orbitals including an empty sphere at $(.5\ .5\ .5)a$. Both cases include core excitations.

Figure 7

The loss spectra of Si with local field (solid line) and without local field (dotted line), calculated with $3s$, $3p$, $3d$, $4f$ orbitals and with a Gaussian broadening $\sigma = 0.1\ Ry$. Core excitations are included. The solid circles are the experimental result.