Optimized effective potential method with exact exchange and static RPA correlation

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Abstract

We present a new density-functional method of the self-consistent electronic-structure calculation which does not exploit any local density approximations (LDA). We use the exchange-correlation energy which consists of the exact exchange and the correlation energies in the random-phase approximation. The functional derivative of the correlation energy with respect to the density is obtained within a static approximation. For transition metals, it is shown that the correlation potential gives rise to a large contribution which has the opposite sign to the exchange potential. Resulting eigenvalue dispersions and the magnetic moments are very close to those of LDA’s and the experiments.

71.10.-w, 71.15.Mb, 71.45.Gm
The optimized-effective-potential (OEP) method for the electronic-structure calculations was first applied to atoms by Talman and Shadwick [1], who recognized it as a kind of restricted minimum search for the Hartree-Fock total energy. In the method, the variational space was restricted to the space of the local one-particle potential, which generates all the eigenfunctions, or to the space of the corresponding density. From the view of the density-functional (DF) theory, their calculations are recognized as the Kohn-Sham (KS) exact exchange (EXX) -only DF calculations. In the last years, we have extended their method to be applicable for solids [2]-[4], where we add the correlation energy in the local density approximation (LDA). As was shown there, the results admittedly were not satisfactory from the view point of comparison with experiments. Especially for transition metals such as iron [3], the method gave the occupied \(d\) bands which were too deep relative to the \(s\) bands and also gave rise to too large magnetizations. This indicates that the LDA correlation is poor when we combine it with EXX, and that the true correlation should give rather large contributions cancelling large EXX.

There are two kinds of way to take into account the correlation energy more precisely. One is the multiple-configuration extension [5], which is a widely-used idea in the quantum chemistry. The other is based on the DF theory, to utilize the implicit DF for the correlation energy based on the KS orbitals, in addition to the EXX energy. Along the second, Garbo and Gross tried a new DF for correlation, which applied to atoms and molecules [6].

In this Letter, we present a new method for solid along the second line. We use an exchange-correlation (XC) energy functional, which consists of the EXX energy and a correlation energy in the random-phase approximation (RPA). The correlation potential, which is the functional derivative of the correlation energy with respect to the density, is evaluated within a static approximation; the static screened-Coulomb interaction, which is used for the evaluation of the RPA correlation, is calculated by use of the product-basis method developed by Aryasetiawan and Gunnarson [7]. We denote our method as EXX+RPA in the following.

Formally, the XC energy \(E_{xc}[n]\) as a DF is given by use of the coupling-integral method:
\[ E_{xc}[n] = \frac{e^2}{2} \sum_{\sigma,\sigma'} \int_0^1 d\lambda \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\langle \hat{\psi}^\dagger_{\sigma}(\mathbf{r}_1) \hat{\psi}^\dagger_{\sigma'}(\mathbf{r}_2) \hat{\psi}_{\sigma'}(\mathbf{r}_2) \hat{\psi}_{\sigma}(\mathbf{r}_1) \rangle_{n,\lambda} - n_\sigma(\mathbf{r}_1)n_{\sigma'}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \]  

(1)

where \( \hat{\psi} \) denotes the electron field operator, and \( \langle ... \rangle_{n,\lambda} \) indicates the vacuum expectation value with respect to the system with the given density \( n_\sigma(\mathbf{r}) \) and the coupling \( \lambda e^2 \). Note that the given density is kept unchanged for any \( \lambda \) by applying the \( \lambda \)-dependent external potential. The EXX energy \( E_{xc}[n] \) as a functional of the density is defined as the \( e^2 \) term of \( E_{xc}[n] \). As a correlation energy functional \( E_c[n] \), we only take the RPA contribution included in the expression of Eq.(1):

\[ E_{c,\text{RPA}}[n] = \frac{i}{2} \int_0^1 \frac{d\lambda}{\lambda} \text{Tr}[(1 - v_\lambda D^0)^{-1} v_\lambda D^0 - v_\lambda D^0] = -\frac{i}{2} \text{Tr}[\log(1 - vD^0) + vD^0], \]  

(2)

\[ D^0_\sigma(\mathbf{r}_1, \mathbf{r}_2, \omega) = \sum_{\text{occ.}} \sum_{\text{unocc.}} \psi^i_\sigma(\mathbf{r}_1) \psi^j_\sigma(\mathbf{r}_2) \psi^{j*}_\sigma(\mathbf{r}_2) \psi^i_\sigma(\mathbf{r}_1) \left\{ \frac{1}{\omega - \epsilon^i_\sigma + \epsilon^j_\sigma + i\delta} - \frac{1}{\omega + \epsilon^i_\sigma - \epsilon^j_\sigma - i\delta} \right\}, \]  

(3)

where the trace is taken for index \( 1 \equiv \mathbf{r}t\sigma \) (in Eq.(2), we suppress a factor \( 1/\int_{-\infty}^{\infty} dt \) for simplicity). \( v_\lambda \) is defined as \( v_\lambda(1, 2) = \lambda e^2 \delta(t_1 - t_2) \delta_{\sigma_1 \sigma_2}/|\mathbf{r}_1 - \mathbf{r}_2| \), and \( v \) denotes \( v_{\lambda=1} \). Formally, Eq.(2) is the same as that for the RPA correlation energy of the homogeneous electron gas \[8\] except that \( E_{c,\text{RPA}} \) should be treated as a functional of density \( n_\sigma(\mathbf{r}) \) through the Lindhard dielectric function \( D^0_\sigma \), which is spin-diagonal and constructed from the eigenfunctions \( \psi^i_\sigma(\mathbf{r}) \) satisfying

\[ \left[ -\nabla^2 + V^\text{eff}_\sigma(\mathbf{r}) - \epsilon^i_\sigma \right] \psi^i_\sigma(\mathbf{r}) = 0, \]  

(4)

\[ n_\sigma(\mathbf{r}) = \sum_{\text{occ.}} |\psi^i_\sigma(\mathbf{r})|^2. \]  

(5)

Under the assumption of one-to-one correspondence between \( n_\sigma(\mathbf{r}) \) and \( V^\text{eff}_\sigma(\mathbf{r}) \) (we define \( V^\text{eff} \) so that the chemical potential is included in it), we can treat \( \psi^i_\sigma(\mathbf{r}) \), and hence \( E_{c,\text{RPA}} \), as a functional of \( n_\sigma(\mathbf{r}) \). The approximation of Eq.(2) was suggested by Gross, Dobson and Petersilka in Ref. \[9\] (we omit the term \( f_{xc} \) corresponding to the vertex correction).

The derivative \( \delta E_c \) with respect to \( \delta D^0 \) can be written as

\[ \delta E_c = \frac{i}{2} \text{Tr}[W_p \delta D^0], \]  

(6)

\[ W_p = v_{sc} - v, \]  

(7)
where \( v_{sc} \equiv (1 - v D^0)^{-1} v \) denotes the dynamical screened Coulomb interaction in RPA. We evaluate \( \delta E_c \) in a static approximation, i.e., we replace \( W_p(r_1, r_2, t_1 - t_2) \) with \( W_p^{\omega=0}(r_1, r_2) \times \delta(t_1 - t_2) \), where we define \( W_p^{\omega=0}(r_1, r_2) \equiv \int_{-\infty}^{\infty} dt W_p(r_1, r_2, t) \). This approximation is justifiable if the relaxation time of the dynamical screening \( v_{sc} \), typically the plasma oscillation time-scale, is sufficiently shorter than that of the density fluctuation \( i D^0 \).

We know \( i D^0_\sigma(r_1, r_2, t_1 = t_2) = n_\sigma(r_1)\delta(r_1 - r_2) - [n_\sigma(r_1, r_2)]^2 \). Here we use the non-local density \( n_\sigma(r_1, r_2) \equiv \sum_i^{\text{occ.}} \psi_i^\dagger(r_1) \psi_i^\sigma(r_2) \). Then we obtain \( \delta E_c = \delta E_{c1} + \delta E_{c2} \), where we define

\[
\delta E_{c1} \equiv -\frac{1}{2} \sum_{\sigma} \int d r_1 d r_2 W_p^{\omega=0}(r_1, r_2) \delta([n_\sigma(r_1, r_2)]^2),
\]

\[
\delta E_{c2} \equiv \frac{1}{2} \sum_{\sigma} \int d r W_p^{\omega=0}(r, r) \delta n_\sigma(r).
\]

\( \delta E_{c1} \) and \( \delta E_{c2} \) correspond to the correlated part of the screened exchange and the Coulomb-hole terms, respectively (see p.40 in Ref. [11]). As for \( \delta E_{c1} \), we can calculate its functional derivative \( \delta E_{c1}/\delta V_\sigma^{\text{eff}}(r) \) from \( W_p^{\omega=0}(r_1, r_2) \), \( n_\sigma(r_1, r_2) \) and \( \delta n_\sigma(r_1, r_2)/\delta V_\sigma^{\text{eff}}(r) \) through Eq. (8). Then we obtain \( \delta E_{c1}/\delta n_\sigma(r) \) by the same inversion method as was used to obtain \( \delta E_c/\delta n_\sigma(r) \) (see Eq. (11)). If we evaluate \( \delta E_c \) from Eq. (6) without the static approximation, we obtain the result essentially equivalent to Eq. (27) in Ref. [11], which was used by Godby, Shluter and Sham to discuss the eigenvalues of the density functional theory beyond LDA.

In order to calculate all the related quantities, we exploit the atomic sphere approximation (ASA). Any points in the space are denoted by \((r, R)\), where \( R \) is the index for atomic sphere (AS) and \( r = (r, \theta, \phi) \) is a vector denoting the position in each AS. We consider \( E_{sc}[n^s] \) as a functional of \( n^s_\sigma(r, R) \), where \( n^s_\sigma(r, R) \) denotes the spherically-averaged density. \( W_p^{\omega=0} \) are calculated by the product-basis method [7] as

\[
W_p^{\omega=0}(r_1, R_1, r_2, R_2) = \sum_{i,j} W_p^{\omega=0}(i, R_1, j, R_2) \tilde{B}_i(r_1) \tilde{B}_j(r_2),
\]

where \( \tilde{B}_i(r) \)'s form the product basis (see Ref. [4] for notation). In the method of the LMTO-ASA [12], the non-local density \( n_\sigma(r_1, R_1, r_2, R_2) \) is given as a functional of \( V_\sigma^{\text{eff}}(r, R) \) through the potential parameters and radial basis functions. Therefore \( \delta E_{c1}/\delta V_\sigma^{\text{eff}}(r, R) \) can
be evaluated by use of the derivative chain rule in the same manner used for $E_x$ \[2\]. Now, we can calculate the contribution to the correlation potential $V_{c1}^{\sigma}(r, R) \equiv \frac{\delta E_{c1}[n^\sigma]}{\delta n^\sigma(r, R)}$ by the inversion equation,

$$
\frac{\delta E_{c1}}{\delta V_{\text{eff}}^{\sigma}(r, R)} = \sum_{R'} \int_{0}^{R'} dr' \frac{\delta n^\sigma(r', R')}{\delta V_{\text{eff}}^{\sigma}(r, R)} \times \frac{\delta E_{c1}[n^\sigma]}{\delta n^\sigma(r', R')}.
$$  \[11\]

Eq. \[11\] is essentially the same as the one for $E_x$ in Ref. \[2\]. Adding spin-independent $V_{c2}^{\sigma}(r, R) \equiv (\text{spherically-averaged } W_{\omega=0}^{\sigma}(r, R, r, R))$, we obtain the RPA correlation potential $V_c$. Since we treat only metals, we can determine constant parts of $V_x$ and $V_{c1}$ uniquely (note that $V_{\text{eff}}$ includes the chemical potential). We have developed a code to perform the non-relativistic self-consistent calculation with $V_c$ together with $V_x$. This is done by combining two codes, one calculating $W_p$ and the other LMTO-ASA EXX code; the former is a part of the GW program \[13\] \[14\] provided by Aryasetiawan, and the latter is developed starting from LMTO-4 \[15\].

We show results for Cu(fcc), Ni(fcc), Fe(bcc), and Co(fcc) with the lattice constants determined by LDA, 6.76, 6.55, 5.27, and 6.54 a.u. \[16\], respectively. For the evaluation of $\delta E_x$ and $\delta E_c$, we take all the pairs $(R_1, R_2)$ within the second nearest neighbors and treat $4s$, $4p$, and $3d$ as valence orbitals. For the calculation of $W_{\omega=0}^{\sigma}$, we use 35-$k$ points in the irreducible Brillouin zone, with the Lorenzian broadening $\delta = 0.02$ Ry. in Eq. \[3\]. We used 90 optimum product basis $B_i$’s, where all the core eigenfunctions are used to generate them.

In Fig. \[1\], we show the self-consistent $V_{xc} = V_x + V_{c1} + V_{c2}$ for Cu, Ni, and Fe. Constant parts of $V_x$ and $V_{c1}$ are properly fixed for presentation. We find that the large dips of $V_x$ and the large differences between up- and down-spin components of $V_x$ are strongly reduced by adding $V_c$. As a result the final $V_{xc}$ obtained by EXX+RPA gets much closer to those by LDA \[17\] than it was for $V_x$ obtained by EXX. $V_{c2}$, which corresponds to the screening length \[18\], has considerable structures but its contribution to $V_c$ is largely cancelled by $V_{c1}$ in the vicinity of the core region. This can be explained by the fact that $\delta n(r_1, r_2)$ is sufficiently short-ranged for given $\delta n(r)$ near the core region, which allows us to evaluate $\delta E_c$ approximately by use of $W_{\omega=0}^{\sigma}(r_1, r_1)$ instead of $W_{\omega=0}^{\sigma}(r_1, r_2)$ in Eqs. \[8-9\]: By this
replacement, we have $\delta E_{c1} + \delta E_{c2} = 0$ because of $\int d\mathbf{r}_1 D^0_\sigma(\mathbf{r}_1, \mathbf{r}_2, t_1 = t_2) = 0$. On the other hand, we see a rather large cancellation between $V^x$ and $V^{c1}$ out of the core region ($r \gtrsim 1.0$ a.u.). This is because the main contribution to $\delta E_{c1}$ in Eq.(8) comes from the integral out of the range of $v_{sc}^{\omega=0}$, where we expect the behavior of $W^\omega_{p=0}(r_1, r_2) \sim -1/|r_1 - r_2|$.

The eigenvalue dispersions are shown in Fig.2 together with those calculated by usual LDA, and EXX. Results by EXX+RPA are very close to those obtained by LDA, and are much different from the results by EXX. The magnetic moments shown in Table I are also in good agreement with the LDA’s and experiments. To obtain numerically accurate values of the magnetic moments, it is necessary to extrapolate the series of fully converged (about the number of $k$ points) results for different $\delta$ towards $\delta = 0$. This, however, seems too time-consuming in the present stage of our unoptimized computer code, and we only show the results for $\delta = 0.04$ Ry. with 35-$k$ points in Table I for reference.

Let us discuss some possible sources of the difference between our results and those of the true DF. These are (1) the product-basis expansion, (2) RPA, and (3) static approximation for RPA. As for (1), our test for a model interaction $v_{sc} = \exp(-\kappa r)/r$ (in this case we can obtain accurate results without using the product-basis expansion) indicates that the potential $V_c$ is poorer when getting closer to the AS’s center. The oscillation of $V_c$ near the nucleus seems to be an artifact due to the method of expansion. However, this fortunately little affects on the energy bands and the magnetic moments (we will show the details in the subsequent paper). To take into account the effects beyond RPA, (2), we have to treat $f_{xc}$ in Ref. [9], which corresponds to the vertex correction. Some parts of the contribution due to $f_{xc}$ might be taken into account by LDA-like approximations; one of the simple ways is to add the difference between the LDA XC calculated by RPA [17] and the one calculated by a more accurate scheme [19]. We tried the above method but the correction turned out to be rather small; the magnetization of Fe enhanced by 0.05 $\mu_B$ (this value is similar to the corresponding LDA case). However, we are not so confident whether the correction is really meaningful or not. As for (3), the dynamical effects will be simulated in effect by making $v_{sc}^{\omega=0}$ closer to $v$ (no relaxation limit). It should reduce the magnitude of $V_c$. Therefore
the position of $d$ band relative to $s$ band should be somehow pushed down for Cu case (See Fig.1). Contrary, this estimation concerning (3) is opposite in the case of LDA. In the case of LDA, we can rather easily show that $d$ bands calculated by LDA in the RPA [17] are pushed up from those obtained by its static approximation. In conclusion, it seems rather difficult to evaluate (3) based on the LDA idea; we have not succeeded in giving any reasonable evaluations for the magnitude of errors due to (2) and (3).

It sometimes have been claimed that the itinerant-magnetism is a sensitive problem where the higher-order electron-correlation [20] beyond RPA screening might be essential in determining the magnetic moments or the ground states. Our results, however, indicate that the essential part determining the magnetic moments might be well accounted for by the correlation within the RPA screening, even though the higher-order correlations are certainly important for excitations as was discussed in Ref. [13]. Incidentally, as for the the higher-order correlations, we as well can extend the OEP method to include other classes of correlation diagrams included in Eq.(1) and to evaluate their contributions in an ab-initio way. For example, the exchange diagrams of order $e^4$ that is important to cancel the self-interaction of order $e^4$ can be included. Further, the ladder types of diagrams that include the free energy due to the spin wave should be taken into account in the case of finite temperatures.

Our method determines not only $V_{\text{eff}}$, but also $W_{\omega=0}$ in a self-consistent manner. $W_{\omega=0}$ calculated from the LDA eigenfunctions (and eigenfunctions) seems reasonable for transition metals: For example, the magnetic moments $2.07 \mu_B$ of Fe, which is calculated with a fixed $W_{\omega=0}$ calculated from the LDA eigenvalues, is very close to the self-consistent value $2.04 \mu_B$ in Table I. However, such results obtained by the LDA eigenvalues are not expected to be sufficient for solids like transition-metal oxides. In Ref. [14] for NiO, it is shown that the GW calculation with $W_p$ constructed from the LDA eigenvalues gives poor results because of the too small a LDA band gap, and that the self-consistency of GW is essentially needed. The fully self-consist calculation of GW seems very hard mainly due to the programing difficulties and the lack in computational power. From such a point of views, our self-
consistent calculation might be a good substitution of the self-consistent $GW$.

We have not developed the code to calculate $E_{c}^{\text{RPA}}$ itself yet. We only treated its functional derivative $\delta E_{c}^{\text{RPA}}/\delta n^s$, and the static approximation is not applicable for the total energy calculation. To our knowledge, none have done the ab-initio calculation of $E_{c}^{\text{RPA}}$. It requires to treat unoccupied states precisely. It might be a little difficult in LMTO-ASA scheme. However, we have to try such calculations for determining lattice constants and other cohesive properties.

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REFERENCES

[1] J. D. Talman and W. F. Shadwick, Phys. Rev. A14, 36 (1976).

[2] T. Kotani, Phys. Rev. Lett. 74 2989 (1995); Phys. Rev. B 50 14816 (1994), ibid. 51 13903(E) (1995); T. Kotani and H. Akai, ibid. 52 17153 (1995);

[3] T. Kotani and H. Akai, Physica B in press.

[4] T. Kotani and H. Akai, Phys. Rev. B 54 16502 (1996).

[5] K. Aashamar, T. M. Luke, and J. D. Talman, J. Phys. B 12, 3455 (1979).

[6] T. Garbo, and E. K. U. Gross, Chem. Phys. Lett. 240, 141 (1995); to appear in Int. J. Qua. Chem. (1997).

[7] F. Aryasetiawan and O. Gunnarson, Phys. Rev. B 49, 16214 (1994).

[8] See, e.g, A. L. Fetter and J. D. Walecka, Quantum Theory of Many-Particle Systems, (McGraw-Hill, New York, 1971).

[9] E.K.U.Gross, J.F. Dobson, and M. Petersilka, in Density functional theory, edited by R.F. Nalewajski, Topics in Current Chemistry, (Springer-Verlag, Berlin Heidelberg, 1996) Vol. 181, p. 81.

[10] L. Hedin and S. Lundqvist, in Solid State Physics, edited by H. Ehnrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 1.

[11] R. W. Godby, M. Shluter, and L. J. Sham, Phys. Rev. B 37, 10159 (1988);

[12] O. K. Andersen, O. Jepsen, and D. Glötzel, in Highlights of Condensed-Matter Theory, edited by F.Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985), p.59;

[13] F. Aryasetiawan, Phys. Rev. B 46, 13051 (1992);

[14] F. Aryasetiawan and O. Gunnarson, Phys. Rev. Lett 74, 3221 (1995), F. Aryasetiawan and K. Karlsson, Phys. Rev. B 54, 5353 (1996)
[15] The TB-LMTO program ver. 4, by M. van Schilfgaarde, T. A. Paxton, O. Jepsen, and O. K. Andersen, Max-Planck-Institut für Festkörperforschung, Federal Republic of Germany, (1992)

[16] V. L. Moruzzi, J. F. Janak, and A. R. Williams, Calculated Electronic Properties of Metals, (Pergamon press inc., New York, 1971).

[17] The RPA-level of LDA by U. von Barth and L. Hedin, J. Phys. C5, 1629 (1972).

[18] If we assume a simple-form for the screening, i.e., \( v_{sc}^{\omega=0}(r_1, r_2) = \exp(-\kappa |r_1 - r_2|)/|r_1 - r_2| \), we can set \( V^{c2} = -\kappa \) following its definition.

[19] S. H. Vosko, L. Wilk, and M Nusair, Can. J. Phys. 58, 1200, (1980)

[20] J. Kanamori, Prog. Theor. Phys. 30, 275 (1963)

[21] R. A. Reck and D. J. Fry, Phys. Rev. 184, 492 (1969); H. Denan, A. Herr, and A. J. P. Meyer, Jour. App. Phys. 39, 69 (1968); M. J. Besnus, A. J. P. Meyer, and R. Berninger, Phys. Lett. 32A, 192 (1970)
FIGURES

FIG. 1. Exact exchange potential $V^x$ and RPA correlation potential $V^c = V^{c1} + V^{c2}$ for Cu, Ni and Fe. The LDA XC potential $^{[17]}$ as references are calculated for the density determined by the self-consistent calculation of EXX+RPA.

FIG. 2. Energy dispersion curves calculated by three different types of self-consistent calculations, LDA, EXX, and EXX+RPA. EXX denotes the calculation which is performed with LDA correlation $^{[17]}$ potential in addition to the EXX potential.
TABLES

TABLE I. Calculated spin magnetic moments ($\mu_B$). For EXX+RPA, we show the values obtained with $\delta = 0.02$ Ry, and $\delta = 0.04$ Ry (parenthesis), see Eq.(3). The lattice constants used in the calculations are somehow smaller than the experimental ones (see text). Experimental spin magnetic moments are deduced from the experimental values of the saturated magnetization and g-values [21].

|     | LDA  | EXX  | EXX+RPA | Expt. |
|-----|------|------|---------|-------|
| Fe  | 2.13 | 3.27 | 2.04 (2.07) | 2.12  |
| Co  | 1.54 | 2.29 | 1.51 (1.52) | 1.59  |
| Ni  | 0.58 | 0.68 | 0.57 (0.58) | 0.56  |
**Fig. 1(a)**
\begin{align*}
V_{xc}^{\text{up}} + V_{xc}^{\text{down}} &= \frac{V_{xc}^{\text{up}} + V_{xc}^{\text{down}}}{2} \\
V_{xc}^{\text{up}} - V_{xc}^{\text{down}} &= \frac{V_{xc}^{\text{up}} - V_{xc}^{\text{down}}}{2}
\end{align*}

RPA Correlation potential

\[ V_c = V_{c1} + V_{c2} \]

Up spin

Down Spin

Exact exchange \( V_x \)
Energy (Ry)

EXX+RPA
LDA

\[ \frac{V_{xc}^{\text{up}} + V_{xc}^{\text{down}}}{2} \]

Energy (Ry)

RPA Correlation potential

\[ V_c = V_{c1} + V_{c2} \]

\[ V_{c1} \]

\[ V_{c2} \]

Exact exchange \( V_x \)

Fig. 1 (c)
Fig. 2