

Self-consistent Hartree-Fock and screened-exchange calculations in solids: Application to silicon

F. Gygi

Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

A. Baldereschi

*Institut de Physique Appliquée, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
and Istituto di Fisica Teorica, University of Trieste, Trieste, Italy*

(Received 3 December 1985; revised manuscript received 7 July 1986)

A simple procedure to perform Hartree-Fock calculations in solids using extended basis functions is proposed. The method also applies when correlation is added with the self-consistent Coulomb-hole-plus-screened-exchange (COHSEX) scheme. Application to silicon in the pseudopotential approach yields excitation energies which agree with recent results by Hybertsen and Louie. We find that the simple diagonal COHSEX approximation does not provide satisfactory indirect excitation energies in silicon but is quite accurate for the direct ones.

The local-density approximation (LDA) to density-functional theory¹ has proved to be a powerful tool for accurate studies of ground-state properties of solids. Excitation energies, however, cannot be investigated on the same footing since, besides the errors due to the use of LDA, the eigenvalues of the Kohn-Sham density-functional equations cannot be interpreted as quasiparticle energies. For semiconductors, for example, the LDA energy gaps are substantially smaller than experimental data. Several extensions of LDA, such as nonlocal-density approximations,² or energy-dependent functionals³ have been proposed for the excitation energies. The best results, however, have been obtained from calculations^{4,5} based on many-body perturbation theory which include exchange and correlation with the GW approximation of Hedin.⁶ The full dynamical character of the many-body interaction is included, and the results compare well with experiment for diamond, Si, and LiCl. These calculations are extremely time consuming and therefore have been limited to a few materials only. An analytical self-energy model has recently been proposed in an attempt to simplify the computations.⁷

In this work, we present a procedure which allows one to calculate GW quasiparticle energies with a reduced numerical effort using a plane-wave basis set. The method is particularly simple in the limiting case of the Hartree-Fock approximation where the self-energy reduces to the exchange operator. The soundness of the technique is demonstrated by calculating the quasiparticle energies of silicon with two different approximations: the Hartree-Fock and the diagonal Coulomb-hole-plus-screened-exchange (COHSEX) schemes.

For convenience, we describe the technique for the Hartree-Fock self-energy operator Σ_{HF} . In this case, the self-consistent band-structure calculation involves exchange matrix elements of the type

$$\langle f | \Sigma_{\text{HF}} | g \rangle = -e^2 \sum_{m,q} \int \frac{f^*(\mathbf{r}) \phi_{mq}^*(\mathbf{r}') \phi_{mq}(\mathbf{r}) g(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}', \quad (1)$$

where the sum is over all occupied Bloch orbitals ϕ_{mq} and f and g are basis functions. Using the decomposition of ϕ_{mq} in plane waves,

$$\phi_{mq}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{mq}(\mathbf{G}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}, \quad (2)$$

and plane waves as basis functions, the exchange matrix element becomes

$$\begin{aligned} \langle \mathbf{k}+\mathbf{G} | \Sigma_{\text{HF}} | \mathbf{k}+\mathbf{G}' \rangle \\ = -\frac{4\pi e^2}{\Omega} \sum_{m,q} \sum_{\mathbf{G}''} \frac{c_{mq}^*(\mathbf{G}'+\mathbf{G}'') c_{mq}(\mathbf{G}+\mathbf{G}'')}{|\mathbf{k}-\mathbf{q}-\mathbf{G}''|^2}. \end{aligned} \quad (3)$$

Evaluation of expression (3) is the time-consuming step in the Hartree-Fock computation. The expression contains a sum over occupied states and requires the knowledge of Bloch functions everywhere in the Brillouin zone. Direct summation by the special-point technique does not apply since the summand has an integrable divergence for $\mathbf{k}-\mathbf{q}=\mathbf{G}_0$ (a reciprocal-lattice vector) of the form

$$\frac{c_{m\mathbf{k}-\mathbf{G}_0}^*(\mathbf{G}'+\mathbf{G}_0) c_{m\mathbf{k}-\mathbf{G}_0}(\mathbf{G}+\mathbf{G}_0)}{|\mathbf{k}-\mathbf{q}-\mathbf{G}_0|^2} = \frac{c_{m\mathbf{k}}^*(\mathbf{G}') c_{m\mathbf{k}}(\mathbf{G})}{|\mathbf{k}-\mathbf{q}-\mathbf{G}_0|^2}, \quad (4)$$

where the equality comes from the fact that Bloch functions at equivalent wave vectors represent the same state.

The difficulty can be removed by adding and subtracting to the right-hand side (rhs) of (3) a reference term which has the same singularities as the exact expression, i.e., by writing the matrix element as

$$\langle \mathbf{k} + \mathbf{G} | \Sigma_{\text{HF}} | \mathbf{k} + \mathbf{G}' \rangle = - \frac{4\pi e^2}{\Omega} \left[\sum_{m, \mathbf{q}} \left[\sum_{\mathbf{G}''} \frac{c_{m\mathbf{q}}^* (\mathbf{G}' + \mathbf{G}'') c_{m\mathbf{q}} (\mathbf{G} + \mathbf{G}'')}{|\mathbf{k} - \mathbf{q} - \mathbf{G}''|^2} - c_{m\mathbf{k}}^* (\mathbf{G}') c_{m\mathbf{k}} (\mathbf{G}) F(\mathbf{k} - \mathbf{q}) \right] + \sum_m c_{m\mathbf{k}}^* (\mathbf{G}') c_{m\mathbf{k}} (\mathbf{G}) \sum_{\mathbf{q}} F(\mathbf{k} - \mathbf{q}) \right], \quad (5)$$

where $F(\mathbf{p})$ is an auxiliary periodic function that diverges like $1/p^2$ as p vanishes. The term in large parentheses on the rhs is regular and can be evaluated by the special-point technique, whereas the integral which appears in the last term of the rhs is independent of \mathbf{k} [since $F(\mathbf{p})$ is a periodic function] and can be easily evaluated once a convenient auxiliary function $F(\mathbf{p})$ has been specified. The choice of $F(\mathbf{p})$ is not critical except for the fact that, away from its divergences, it must be smooth enough for the application of the special-point technique.

Since the matrix elements of the kinetic energy, of the bare potential, and of the Hartree potential are easily calculated in a plane-wave basis set, this technique allows one to compute easily the matrix elements of the Fock operator everywhere in the Brillouin zone and, by iteration, to obtain Hartree-Fock energy bands. The technique, described here for Σ_{HF} , can also be applied if one uses more elaborate approximations than Hartree-Fock. An application of this kind will be described later in this paper.

$$F(\mathbf{p}) = \frac{(a/2)^2}{3 - \cos(ap_x/2) \cos(ap_y/2) - \cos(ap_y/2) \cos(ap_z/2) - \cos(ap_x/2) \cos(ap_x/2)}, \quad (6)$$

which reflects the fcc periodicity of the lattice. Its mean value in the Brillouin zone (BZ) is

$$\frac{\Omega}{(2\pi)^3} \int_{\text{BZ}} d^3p F(\mathbf{p}) = \left(\frac{a}{2\pi} \right)^2 \sqrt{3} K^2 \left[\sin \left(\frac{\pi}{12} \right) \right] = \left(\frac{a}{2\pi} \right)^2 4.423758, \quad (7)$$

where $K(x)$ is the complete elliptic integral of the first kind. The smooth part of the exchange matrix elements, i.e., the term in large parentheses on the rhs of (5), was calculated with the single mean-value point technique. The Hartree-Fock energies of the most important states are given in Table II. Convergence tests with two mean-value points show that the accuracy of these values is

TABLE I. Hartree-Fock pseudopotential of the Si^{4+} ion. The notation of the parameters is the same as in Ref. 8. We have used $a(\text{core}) = 2.00$, $a(\text{core}) = 1.00$, and $a(5) = a(6) = 0$ for all angular momenta. All values are in atomic units.

	$l=0$	$l=1$	$l=2$
$\alpha(1)$	1.00000	1.37500	3.70000
$\alpha(2)$	3.47535	2.50100	3.73000
$a(1)$	1.30077518	3.20829776	337682.25781250
$a(2)$	12.26687221	4.41675764	-337686.17187500
$a(3)$	-0.42976021	-0.71499994	-4789.81884766
$a(4)$	30.99871189	3.18848371	-5367.83227539

We have applied the technique to the calculation of the Hartree-Fock and screened-exchange energy bands of silicon, since the excitation energies of this material have recently been discussed in detail within various approximations.^{4,5} We use a nonlocal norm-conserving pseudopotential that we have constructed following the procedure of Bachelet, Hamann, and Schlüter.⁸ For consistency in the treatment of many-body interactions, the potential was derived from the Hartree-Fock valence energies and orbitals of a Si^{3+} ion. The resulting pseudopotential (see Table I) gives LDA energy bands which are similar to those obtained with the pseudopotential of Ref. 8, even though the latter has been derived from the neutral Si atom using the local-density approximation.

The Hartree-Fock calculation was performed including plane waves with energy up to 19.5 Ry. The exchange matrix elements were calculated for a limited part of the Fock matrix corresponding to an energy cutoff of 15 Ry, using the auxiliary function

better than 0.2 eV. We find, for example, that, upon going from one to two mean-value points, the E_0 and E'_0 energy gaps change by +0.07 and -0.06 eV, respectively. Hartree-Fock energy bands of silicon have been previously calculated by Dovesi, Causa, and Angonoa⁹ and Ohkoshi.¹⁰

TABLE II. Principal band energies in Si obtained with different approximations and compared with experimental values. The d-COHSEX values from Hybertsen and Louie have been estimated from Fig. 1 of Ref. 5. Energies are given in eV and measured with respect to the valence-band maximum.

	HF	d-COHSEX	d-COHSEX (perturbation)	Expt.	LDA
Γ_{15c}	9.27 ^a	3.24	3.20	3.4 ^b	2.55
Γ'_{2c}	11.04 ^c	4.41	4.43	4.2 ^b	3.40
X_{1c}	6.87	0.83	0.75	1.3 ^d	0.61
L_{1c}	8.13	2.14	2.08	2.1 ^c	2.4 ^f
L_{3c}	10.16	3.97	3.93	4.1 ^f	3.33
E_g	6.43 ^g	0.68 ^h	0.60	1.17 ^b	0.48
$L_{1c} - L_{3'v}$	9.61	3.48 ⁱ	3.46	3.5 ^b	3.9 ^f
$X_{1c} - X_{4v}$	10.71	4.19	4.20	4.2 ^d	4.5 ^b

^a8.15 in Ref. 10.

^fReference 14.

^bReference 13.

^g5.8 in Ref. 10.

^c9.40 in Ref. 9.

^h0.52 in Ref. 5.

^dReference 2.

ⁱ3.28 in Ref. 5.

^eReference 15.

Our Hartree-Fock band structure differs appreciably from that by Dovesi *et al.*, and this is probably due to an inadequate convergence of the latter calculation as discussed by the authors themselves. Better agreement exists with the results by Ohkoshi. His valence-band structure agrees with ours within 0.2 eV which is a remarkable result if one considers that the two calculations use different cutoff energies and different pseudopotentials. However, important differences (about 1 eV and therefore well outside our numerical uncertainty) exist for the valence-to-conduction excitation energies, our values being systematically larger. We attribute these differences to a numerical inaccuracy in the Brillouin-zone integration of the exchange divergence in the work by Ohkoshi. With the use of 10 mean-value points, Ohkoshi evaluates accurately the regular part of the exchange matrix elements given in the term in large parentheses in (5), but not the singular part. We have, in fact, integrated over the Brillouin zone the auxiliary function given in (6) using Ohkoshi's smoothing technique and 10 mean-value points, and found only 92% of the exact result given in (7). This result is consistent with Ohkoshi's underestimate of the excitation energies by about 1 eV, since the contribution to the energy gaps from the singular term in (5) amounts to about 15 eV.

We also report in Table II experimental energy-band levels. As usual, Hartree-Fock gaps are larger than experimental values by a factor of 2 or more. However, Hartree-Fock calculations are the reference for a proper evaluation of correlation effects. In this work we include correlation through a simplified version of the *GW* approximation. We use the diagonal COHSEX (d-COHSEX) approximation, which was already used by Brinkman and Goodman¹¹ in their pioneering work on the effects of correlation on the energy bands of valence semiconductors. It consists of considering only static diagonal screening [i.e., $\epsilon(\mathbf{q}, \mathbf{q}') \sim \epsilon(\mathbf{q}, \mathbf{q})\delta(\mathbf{q}, \mathbf{q}')$] in Hedin's formulation. We use the dielectric function

$$\epsilon(q) = \frac{q^2 + a^2}{q^2 + a^2/\epsilon_0}, \quad (8)$$

with $\epsilon_0 = 11.4$ and $a = 0.93$ a.u., which reproduces the results of RPA calculations.¹² The d-COHSEX approximation neglects local-field and dynamic screening effects which contribute appreciably to the energy gaps in Si.⁵ Our goal here is to present a second application of our procedure and to stress that its use is not limited to Hartree-Fock computations. In the d-COHSEX scheme, the Coulomb potential appearing in expression (3) is replaced by a screened potential, and, accordingly, the auxiliary function $F(\mathbf{p})$ must be scaled by ϵ_0 .

The results of the d-COHSEX calculation are given in Table II and have an accuracy better than 0.1 eV. All Hartree-Fock gaps are reduced by dielectric screening, but the results show that even this approximation is too crude to describe properly the self-energy of silicon. For example, the lowest indirect gap is now considerably underestimated. However, the lowest direct excitation energies, and, in particular, those at *L* and *X* are in satisfactory agreement with experimental data. The agreement with the diagonal COHSEX results of Ref. 5 is good, considering the fact that different dielectric functions and different

TABLE III. Fourier coefficients of the valence charge density in silicon obtained with the various approximations discussed in the text and using the single mean-value point technique. All values are given in electrons per unit cell.

G	Hartree	LDA	d-COHSEX	HF
(1,1,1)	-1.42	-1.67	-1.59	-1.77
(2,2,0)	0.14	0.13	0.14	0.16
(3,1,1)	0.30	0.36	0.35	0.42
(2,2,2)	0.20	0.31	0.29	0.43
(4,0,0)	0.34	0.40	0.38	0.43

pseudopotentials are used in the two calculations.

In order to compare the d-COHSEX and the local-density approximations, a test LDA calculation was performed using our Hartree-Fock (HF) potential and Wigner's interpolation formula for exchange and correlation. The resulting LDA energy gaps, given in Table II, systematically underestimate the experimental data. The d-COHSEX results are generally in better agreement with experiment than the LDA results even if the two schemes underestimate the fundamental indirect gap by comparable amounts.

To conclude, we compare the wave functions obtained with the various approximations discussed above. For valence states, we give in Table III the Fourier coefficients of the valence charge density obtained in the Hartree, Hartree-Fock, d-COHSEX, and LDA approximations. The d-COHSEX charge density is similar to the LDA result, whereas the Hartree and Hartree-Fock densities are quite different from the others. As expected, the Hartree charge density is more diffuse in the unit cell than the LDA one, while the Hartree-Fock charge density is more concentrated at the bond sites. Analysis of wave functions at several points of the Brillouin zone leads to the same conclusion, i.e., the d-COHSEX and LDA approximations provide similar valence wave functions. As an example, we give in Table IV the overlap integrals between corresponding states at the *L* point obtained with the three approximations. The data reported in the table show that the

TABLE IV. Overlap integrals between corresponding states at the *L* point obtained with the Hartree-Fock, d-COHSEX, and LDA approximations. The table gives the deviation of the overlaps from unity in units of 10^{-5} .

	HF vs LDA	LDA vs d-COHSEX	HF vs d-COHSEX
$L_{2'_v}$	20	6	8
L_{1v}	72	10	49
$L_{3'_v}$	50	11	23
L_{1c}	75	81	16
L_{3c}	69	66	1
$L_{2'_c}$	240	414	5

similarity between LDA and d-COHSEX functions does not hold for conduction states, where the d-COHSEX functions are closer to the Hartree-Fock functions than to the LDA ones. These results are important since they show that self-consistent COHSEX (or d-COHSEX) calculations can be avoided if one performs an LDA calculation, approximates Σ_{COHSEX} in terms of LDA functions, and then adds the effects of $(\Sigma_{\text{COHSEX}} - \Sigma_{\text{LDA}})$ in perturbation theory. Results obtained with this perturbation scheme are given in the third column of Table II and show that the deviations in band-gap energies between the fully self-consistent and the perturbation treatment are less than 0.1 eV. Perturbation schemes of this kind have been used in the past by several authors,^{4,5,11} and their validity is confirmed by our results. It is worth mentioning, however, that this approach is not applicable to Hartree-Fock calculations since (i) the difference operator $(\Sigma_{\text{HF}} - \Sigma_{\text{LDA}})$ is not a small perturbation, and (ii) Σ_{HF} cannot be constructed in terms of LDA functions.

Hartree-Fock and improved Hartree-Fock calculations are common for atoms and molecules, but not for solids, since they are extremely time consuming for infinite periodic systems. They have been performed for a few ma-

terials only and, given the numerical complexity, different authors have found, for a given material, quite different results. Moreover, these computations have usually been carried out using localized basis functions, whereas the most convenient functions in solid-state calculations are plane waves or modified plane waves. In this paper we have proposed a procedure that allows one to perform easily Hartree-Fock and improved Hartree-Fock calculations in solids using a plane-wave basis set. With this technique, fully converged Hartree-Fock and COHSEX calculations become feasible with a numerical effort comparable to that of a LDA calculation. These computations can therefore become a common practice in solid-state theory and can be the first step towards the accurate prediction of excitation energies as recent investigations⁵ have demonstrated.

We thank Dr. W. Andreoni, Dr. K. Maschke, and Professor R. Resta for useful comments on the manuscript. This work was supported by the Swiss National Science Foundation, the Troisième Cycle de la Physique en Suisse Romande, and by the Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche.

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