COMMENTS AND ADDENDA

Comment on Pseudopotentials for Transition Metals

Philip B. Allen

Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11790

The Fong—Cohen empirical pseudopotentials for Cu and Nb are shown to be close approximations to a member of a family of pseudopotentials which also includes Harrison's first-principles pseudopotentials for transition metals. The lack of energy dependence in the Fong—Cohen potential is discussed and partly explained.

Fong and Cohen (FC) have recently succeeded in fitting the energy bands of copper[1] and niobium[2] using an empirical pseudopotential. Kleinman[3] has recently discussed this work from the point of view of the cancellation theorem,[4] and emphasized that the lack of energy dependence of the FC parameters is surprising. Kleinman's explanation for FC's success involves a compensating correction to the local part of the potential.

In this comment, an alternate point of view is formulated along the lines of the Austin—Heine—Sham (AHS) "generalized" theory of pseudopotentials.[5] It is argued that the energy independence of the FC parameters can be expected because of the exponential damping of the form factors. As a by-product, a new class of pseudopotentials is found which includes Harrison's[6] first-principles pseudopotentials, making explicit the connection between the work of Fong and Cohen and that of Harrison. The derivation of these new pseudopotentials is done in two stages, one parallel to the Phillips—Kleinman[7] (PK) method, and one parallel to AHS.

Following Harrison[6] in parallel with PK, let us add to the real wave function ψ some fraction α_c of core wave function ψ_c and some fraction α_d of d wave function ψ_d in the hope that the resulting pseudo-wave-function ϕ will have a rapidly convergent plane-wave expansion:

$$\phi = \psi + \sum_c \alpha_c \psi_c + \sum_d \alpha_d \psi_d . \qquad (1)$$

The d wave functions ψ_d (unlike ψ_c) are *not* eigenfunctions of the crystal Hamiltonian H. For convenience, we choose them to be orthogonal to ψ_c, but we *cannot* choose them to be orthogonal to ψ. The function ψ_d is an arbitrary function of d symmetry which is chosen to remove the d-wave part of ψ which otherwise would cause convergence difficulties.

It is now convenient to write ψ as some operator acting on ϕ. If all the coefficients α_d were zero, the usual Pick—Sarma[8] operator $1 - P_c$ would do the job, where

$$P_c = \sum_c |\psi_c\rangle\langle\psi_c| \qquad (2)$$

is a projection operator onto the core subspace. The presence of nonzero α_d's makes the operator more complicated:

$$(1 - P_c - P_d Q)\phi = \psi . \qquad (3)$$

In this formula P_d is the d-wave analog of P_c,

$$P_d = \sum_d |\psi_d\rangle\langle\psi_d| . \qquad (4)$$

The operator Q is defined as any operator such that $P_d Q$ gives zero when acting on ψ but leaves ψ_d unaltered. In addition, $P_d Q$ must give zero when operating on ψ_c. If Q were taken to be the identity operator, Eq. (3) would not be correct because $1 - P_d$ (unlike $1 - P_c$) subtracts off part of ψ. The Schrödinger equation for ψ is

$$(T + V)\psi = \mathcal{H}\psi = E\psi. \qquad (5)$$

This equation is transformed into the pseudo-Schrödinger equation by using Eq. (3):

$$(T + V_p)\phi = E\phi , \tag{6}$$

$$V_p = V + (E - \mathcal{H})(P_c + P_d Q) . \tag{7}$$

The result is a new class of pseudopotentials. As an example, we can recover Harrison's form[6] by making the choice

$$Q = Q_H = \frac{\mathcal{H} - E}{E_d - E} , \quad E_d = \langle \psi_d | \mathcal{H} | \psi_d \rangle . \tag{8}$$

This form for the operator Q is highly energy dependent, having a resonance which would probably be chosen to occur near the energy of the d bands. Less strongly energy-dependent forms could presumably be found.

The preceding discussion was a generalization of the PK method. Let us now generalize the AHS method in an analogous way. Consider the new pseudo-Schrödinger equation:

$$E'\phi = \mathcal{H}_p \phi$$

$$= (T + V + \sum_c |\psi_c\rangle\langle F_c| + \sum_d R|\psi_d\rangle\langle F_d|)\phi \tag{9}$$

In the case $R = 0$, this is just the AHS Hamiltonian, which can be shown to have the same valence spectrum as the real Hamiltonian, $T + V$. Such a Hamiltonian also has spurious solutions belonging to the space of core functions, but presumably such spurious solutions are inaccessible to a computer program which diagonalizes (9) in a truncated plane-wave basis set.

When the operator R is not equal to zero, the pseudo-Hamiltonian has more complicated spectrum. Take the matrix element of (9) with the real wave function ψ on the left. The result is

$$(E' - E)\langle\psi|\phi\rangle = \sum_d \langle\psi|R|\psi_d\rangle\langle F_d|\phi\rangle . \tag{10}$$

The aim is to find a class of operators R such that the valence spectra E' correspond to the valence spectra E of the real Hamiltonian. A sufficient condition is to require the right-hand side of Eq. (10) to vanish, for then we must have either $E = E'$ or ϕ orthogonal to ψ. The latter condition implies that ϕ belongs to the space of core functions, and does not converge rapidly enough in plane waves to be a bothersome possibility. A new and very large family of pseudopotentials is then given by

$$V_p = V + \sum_c |\psi_c\rangle\langle F_c| + \sum_d R|\psi_d\rangle\langle F_d| , \tag{11}$$

where $\langle F_c|$ is arbitrary, and R and $\langle F_d|$ are constrained only by the condition that the right-hand side of Eq. (10) should vanish.

Numerous examples of such pseudopotentials can be found. For example, if $f(x)$ is a function with

the constraint $f(0) = 0$, then a possible form for R is

$$R = f(g(\mathcal{H}) - g(E)) , \tag{12}$$

where the function g is arbitrary. This causes the right-hand side of (10) to vanish. It is also possible to define a pseudo-Hamiltonian self-consistently

$$\mathcal{H}_p = T + V + \sum_c |\psi_c\rangle\langle F_c|$$

$$+ \sum_d f(g(\mathcal{H}_p) - g(E))|\psi_d\rangle\langle F_d| , \tag{13}$$

where the pseudo-Hamiltonian occurs as the argument of g.

Harrison's pseudopotential is now recovered if we take

$$R_H = \frac{\mathcal{H} - E}{E_d - E} , \tag{14}$$

$$\langle F_d|_H = \langle\psi_d|(E - \mathcal{H}) . \tag{15}$$

Fong and Cohen's pseudopotential cannot be found exactly, but a near approximation is found by taking

$$R_{FC} = 1 - \exp[-\beta(\mathcal{H}_p^{1/2} - E^{1/2})^2] ,$$

$$\sum_d |\psi_d\rangle\langle F_d|_{FC} = A(r) P_2 \exp[-\beta(\mathcal{H}_p^{1/2} - E^{1/2})^2] , \tag{16}$$

where $A(r)$ is the radial step function used by FC, P_2 is the $l = 2$ projection operator, and β is the damping parameter of FC. The aim of the empirical method is to have a small secular equation of plane waves, which has mostly plane-wave-type solutions with a parabolic type of dispersion curve, except for the lowest energy solutions which are hybridized d functions with fairly flat bands. The secular equation is dominated by the kinetic energy T, so taking $\mathcal{H}_p = T$ is a good first approximation. If this is done in Eq. (16), as well as setting E equal to a constant corresponding to the kinetic energy of the plane waves which hybridize, then Fong and Cohen's energy-independent, damped, nonlocal form is found.

The validity of these approximations over the width of the d band is hard to assess because numerous plane waves mix to form the hybridized valence bands in Fong and Cohen's calculations. Thus it would be unwarranted to claim that this paper "explains" the success of the Fong–Cohen method. However, this paper does provide a new "language" which interrelates various previously separate trains of thought on transition-metal pseudopotentials.

[1]C. Y. Fong and M. L. Cohen, Phys. Rev. Letters 24, 306 (1970).

[2]C. Y. Fong and M. L. Cohen, Phys. Letters 40A (to be published).

[3]L. Kleinman, Phys. Rev. B 5, 4198 (1972).

[4]M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961); J. B. Pendry, J. Phys. C 4, 427 (1971).

[5]B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. 127, 276 (1962).

[6]W. A. Harrison, Phys. Rev. 181, 1036 (1969).

[7]J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

[8]R. Pick and G. Sarma, Phys. Rev. 135, A1363 (1964).

Hartree–Fock Energy Bands for Argon

Nunzio O. Lipari

Xerox Corporation, Rochester Research Center, Rochester, New York 14603

(Received 8 May 1972)

The energy bands of Ar are investigated in the Hartree–Fock approximation. We have used localized orbitals self-consistent for the crystal (accurate to first order in the interatomic overlap) and the mixed-basis method. The results are compared with previous orthogonalized-plane-wave Hartree–Fock calculations by Lipari and Fowler and augmented-plane-wave calculations by Dagens and Perrot and the agreement is good.

A great deal of effort has been devoted in the past to the calculation of the first-principles energy bands for insulating crystals.[1-4] The role of electronic correlation has been extensively investigated, together with a better understanding of the limits of the Hartree–Fock approximation. The author,[1] in collaboration with Kunz[2] and Fowler[3] has carried out an extensive investigation of both rare gases[1,3] and alkali-halide crystals.[2] The former calculations[1,3] differ from the latter[2] in that in the former we used the orthogonalized-plane-wave (OPW) method together with free-atom wave functions and eigenvalues for the core states, whereas in the latter the mixed-basis (MB) method and localized orbitals[6] were used. Due to these differences, it is hard to compare the two sets of calculations. In particular, it would be interesting to see how much the results will be modified when localized orbitals and the mixed-basis method are used for the rare-gas crystals also. Very recently, Dagens and Perrot[4] have investigated the Hartree–Fock energy bands of argon, using a

method closely related to the classical augumented-plane-wave (APW) method, which treats in a nearly exact way the Hartree–Fock exchange. Their investigation, while confirming our previous main conclusion,[3] finds a smaller separation between the s and d conduction bands with a slightly larger energy gap. Recently, localized orbitals for Ar have been obtained.[7] It seems, therefore, very useful to use these orbitals for an investigation of the energy bands of Ar, since such an investigation could answer some of the above questions.

Since the methods of calculation have been described extensively elsewhere,[2] we will not discuss them here. Very briefly, one first obtains the self-consistent charge density for the crystal, using local orbitals. One then uses the MB method to solve the Hartree–Fock equations.

All the calculations were performed using the Sigma 7 Computer in the Xerox Rochester Technical Computer Center in Webster, New York. The local-orbital core states included in the MB method were the $1s$, $2s$, and $2p$ states. In Table I we

TABLE I. The parameters for Ar are given. See Ref. 7 for the definitions of parameters A_{ij}, Z_{ij}, C_{ijk}, and $\epsilon_{i,j}$. $\epsilon_{1s,1s} = 237.62$, $\epsilon_{1s,2s} = 0.0$, $\epsilon_{2p,2p} = 19.145$, $\epsilon_{2s,2s} = 24.679$, $\epsilon_{1s,2s} = 0.0$, $\epsilon_{3p,3p} = 1.1853$, $\epsilon_{3s,3s} = 2.5616$, $\epsilon_{2s,3s} = 19 \times 10^{-7}$, $\epsilon_{2p,3p} = 21 \times 10^{-7}$.

j	A_{0j}	Z_{0j}	A_{1j}	Z_{1j}	C_{10j}	C_{20j}	C_{30j}	C_{21j}	C_{31j}
1	0	20.750	0	16.220	0.876582	0.230465	0.074527	0.026770	0.005201
2	1	14.900	0	8.230	0.444910	0.220711	0.091844	0.900836	0.246130
3	2	16.500	0	5.000	-0.183197	-0.086199	-0.026546	0.388417	0.098199
4	2	10.500	2	8.000	-0.008064	-0.179010	0.000947	0.192066	0.073941
5	1	6.206	1	2.970	0.005543	-0.926627	-0.479853	0.004425	0.814811
6	2	3.166	2	2.211	-0.001087	-0.007752	0.712572	-0.000737	0.399386
7	2	1.993	1	1.370	0.000473	0.000699	0.497281	0.000340	-0.317584