group VIB 2H-MCh$_2$ compounds,[3,5,6] which agrees with the present APW-LCAO results. Williams and Shephard[6] estimate from their PE data that the occupied 4d bandwidths in 2H-NbSe$_2$ and 2H-MoS$_2$ are less than 0.7 and 1.5 eV, respectively. These are only slightly larger than the calculated widths of 0.5 and 1.0 eV, respectively. These data[4,6] suggest valence p bandwidths of 5–7 eV, which agrees well with the calculated widths of 5.1 and 4.7 eV.

The main discrepancy between the PE data and the present APW results concerns the magnitude of the gap between the M-atom d and the Ch-atom p bands. The PE results indicate that these bands overlap by 0.1–0.2 eV, whereas the APW calculations predict an 0.6–0.7-eV gap. This is certainly the least-reliable aspect of these first-principles calculations. In similar calculations for the transition-metal oxides,[10] it was found that the corresponding p-d gap was overestimated by 1–3 eV. It is believed that these errors are due largely to a lack of self-consistency in the potential and the approximate treatment of exchange and correlation effects.

Finally, it is noted that if the 3p-4d band gap in 2H-MoS$_2$ is reduced by 0.7–0.9 eV, the 3p-4d band overlap of 0.1–0.2 eV will be less than the 4d valence bandwidth of 1.0 eV. As a result, the top of the 2H-MoS$_2$ valence band is still expected to consist of d_{z^2} orbitals at the zone center (Γ_4-). This is consistent with the results of electron paramagnetic resonance studies in p-type 2H-MoS$_2$ samples.[18] Furthermore, it suggests that the A and B excitons that are observed in the 2H-MoS$_2$ transmission spectrum near 2 eV[1] involve d-to-d^9 rather than the previously assigned p-to-$d^{1,7}$ or d-to-p [6] transitions.

---

[1] J. A. Wilson and A. D. Yoffe, Advan. Phys. 18, 193 (1969).

[2] R. H. Williams and A. J. McEvoy, Phys. Status Solidi (b) 47, 217 (1971).

[3] J. C. McMenamin and W. E. Spicer, Phys. Rev. Lett. 29, 1501 (1972).

[4] R. H. Williams, J. M. Thomas, M. Barber, and N. Alford, Chem. Phys. Lett. 17, 142 (1972).

[5] R. H. Williams, J. Phys. C: Proc. Phys. Soc., London 6, L32 (1973).

[6] P. M. Williams and F. R. Shepherd, J. Phys. C: Proc. Phys. Soc., London 6, L36 (1973).

[7] R. A. Bromley, R. B. Murray, and A. D. Yoffe, J. Phys. C: Proc. Phys. Soc., London 5, 759 (1972).

[8] J. B. Goodenough, Mater. Res. Bull. 3, 409 (1968).

[9] R. Huisman, R. DeJonge, C. Haas, and F. Jellinek, J. Solid State Chem. 3, 56 (1971).

[10a] L. F. Mattheiss, Phys. Rev. 181, 987 (1969).

[10b] L. F. Mattheiss, Phys. Rev. B 5, 290 (1972).

[10c] L. F. Mattheiss, Phys. Rev. B 5, 306 (1972).

[10d] L. F. Mattheiss, Phys. Rev. B 6, 4718 (1972).

[11] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1489 (1964).

[12] R. F. Egorov, B. I. Reser, and V. P. Shirokovskii, Phys. Status Solidi 26, 391 (1968).

[13] R. A. Bromley, Phys. Rev. Lett. 29, 357 (1972).

[14] R. Bachmann, H. C. Kirsch, and T. H. Geballe, Solid State Commun. 9, 57 (1971).

[15] M. H. Van Maaren and H. B. Harland, Phys. Lett. 29A, 571 (1969).

[16] E. Ehrenfreund, A. C. Gossard, F. R. Gamble, and T. H. Geballe, J. Appl. Phys. 42, 1491 (1971); M. Marezio, P. D. Dernier, A. Menth, and G. W. Hull, Jr., J. Solid State Chem. 4, 425 (1972).

[17] J. Labbé and J. Friedel, J. Phys. Rad. 27, 153, 303 (1966).

[18] R. S. Title and M. W. Shafer, Phys. Rev. Lett. 28, 808 (1972), and Bull. Amer. Phys. Soc. 18, 47 (1973).

Nonlocal Pseudopotential for Ge

J. C. Phillips and K. C. Pandey*
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 26 January 1973)

Photoemission studies have shown that although energy bands calculated from a three-parameter local pseudopotential agree well with experiment for Si, similar calculations disagree with experiment for Ge by amounts of order 0.5 – 1.0 eV for many states in the valence band. All these discrepancies can be removed through the introduction of one additional parameter describing the effects of 3d core states in Ge.

For many years it has been customary to interpret optical spectra and derive energy bands of semiconductors from local pseudopotentials. The number of parameters needed to specify a satisfactory local pseudopotential is small (approximately three per element making up the crystal), and these are overdetermined by experimental data in the fundamental absorption region. Moreover it has been found that pseudopotential form factors determined in this manner are transferable from one compound to another, and even from semiconductors to metals. The semiempirical local pseudopotential method, because of its simplicity and wide applicability, has for this reason been the most popular method for studying the electronic structure of many metals and semiconductors.[1]

Band calculations based on assumed one-electron potentials (such as the orthogonalized-plane-wave method[2]) correspond to energy-dependent nonlocal pseudopotentials. From studies of model potentials[3] it is known that energy-dependent effects are small, but that nonlocal effects become important for elements such as Ge and Sn which contain d states in the atomic cores. The valence-band densities of states for Si and Ge have recently been studied by Grobman and Eastman,[4] and they have identified a number of edges in the valence band down to and including the lowest state (Γ_1). Their experiments are in good agreement with local pseudopotential calculations[5] for Si (as expected), but show systematic deviations from the calculated values for Ge (because the atomic cores of the latter contain $3d$ states). The deviations are typically of order 0.5–1.0 eV.

Small deviations in conduction-band–valence-band energy differences in Ge (corresponding to edges in the interband density of states) have been known for some time. These suggested to us that we should construct a nonlocal pseudopotential, with the nonlocal parameters determined from the additional information supplied by those edges (in the conventional notation of Cardona these are labeled E_0' and E_1'), whose energies have recently been determined very accurately by modulation spectroscopy. The energy bands derived from the nonlocal potential were then used to calculate the positions of the valence-band edges with no further adjustment of parameters. As expected, the nonlocal values remove all the discrepancies between the local pseudopotential calculations and experiment.

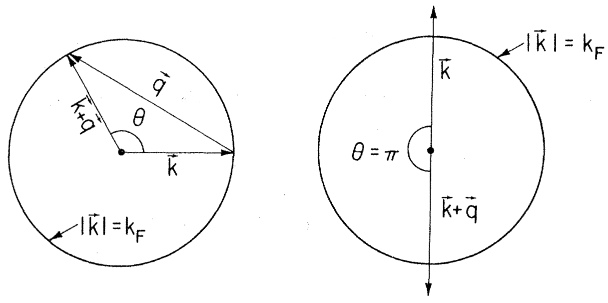

FIG. 1. Choice of states $\vec{k}$ and $\vec{k}+\vec{q}$ for the evaluation of the equivalent local potential $V(q)$ corresponding to nonlocal $V(\vec{k},\vec{k}+\vec{q})$. On the left the case $q \leq 2k_F$ is shown, and on the right $q > 2k_F$. See also Ref. 3, p. 322.

The nonlocal pseudopotential of each atom is written in the form

$$V_{\text{nonl}} = V_{\text{loc}}(r) + \sum_{l=0,2} a_l f_l(R_l) P_l, \tag{1}$$

where $f_l(R)$ is a spherical well of unit depth and radius R_l, and P_l is a projection operator for the partial wave of angular momentum l; a_l is an adjustable constant with dimensions of energy. The equivalent local pseudopotential derived from the nonlocal term in (1) can be calculated using Ziman's on–Fermí-surface definition,[6] as illustrated in Fig. 1. This term has been added to $V_{\text{loc}}(r)$ to give $V_{\text{loc}}^{\text{equiv}}(r)$ as shown in Table I. It is $V_{\text{loc}}^{\text{equiv}}(r)$ that is to be compared with conventional local pseudopotential form factors, which are also shown in Table I.

In choosing to include only s and d partial waves in the nonlocal potential of Eq. (1), we have been guided by two considerations. First, the success of a local pseudopotential in describing the energy bands of Si suggests that the most important

TABLE I. Pseudopotential form factors at various momenta G^2 [in units of $(2\pi/a)^2$ and rydbergs/atom]. First line, crystalline semiempirical local values of Ref. 5. Second line, atomic model potential (Ref. 7). Third line, equivalent local values derived from the present nonlocal pseudopotential; it is the sum of the values from lines 4, 5, and 6. The local part of the present potential is given in line 4. The nonlocal strength parameters for the s and d terms are given in lines 5 and 6, together with the local pseudopotentials derived from the s and d terms. The normalization of the nonlocal strength parameters is chosen so that the matrix element of the s term between constant wave functions normalized to an atomic volume is exactly the strength parameter in rydbergs.

	V_3	V_8	V_{11}	$a_l R_l^3$
V_{CB}	-0.23	0.01	0.06	
V_{mod}	-0.19	0.03	0.07	
$V_{\text{loc}}^{\text{equiv}}$	-0.227	0.021	0.079	
V_{nonl}	-0.222	0.019	0.056	
$V_{\text{nonl}}^{s,\text{ equiv}}$	-0.0005	0.0005	0.0005	5×10^{-4}
$V_{\text{nonl}}^{d,\text{ equiv}}$	-0.0053	0.0018	0.0225	0.164

contribution to the nonlocal pseudopotential in Ge comes from the d states. Second, the s-like states $\Gamma_{2'}$ and L_1 in the conduction band, are known to be very sensitive to changes in crystal potential, e.g., from Si to Ge. Therefore as a check on the calculations the s terms were included separately. However, their effect is shown to be very small, as expected.

Particular attention should be given to the values chosen for R_l. In model potential calculations[7] it has been found that R_M (the model potential core radius, which is l independent) is quite large. However, for the important $l = 2$ term one expects $R_2 > R_M$, because the $3d$ core states are much less tightly bound than the $3s$ and $3p$ core states. On the other hand, the maximum meaningful value of R_l is either r_i, the inscribed sphere radius, or r_w, the atomic or Wigner-Seitz radius. We have carried out calculations for $R_2 = r_i$ and for $R_2 = r_w$, with almost identical results; the values quoted in the table were obtained with $R_2 = r_i$. For R_0 we argue that the important differences between heavier and lighter elements occur near $r = 0$ (relativistic corrections[2]). We have therefore chosen a small value for R_0, and have shown by direct calculation that the results depend only on $a_0 R_0^3$, over a wide range of values of R_0.

The results of our calculations are shown in Table II. The values obtained from the three-parameter local pseudopotential of Cohen and Bergstresser are given in the first column, while experimental values[8-12] are listed in the second column. Our nonlocal values, listed in the third column, are in very good agreement with experiment, and exhibit none of the discrepancies shown by the three-parameter local pseudopotential. One might think that the improvement comes

TABLE II. Experimental values in eV (at low temperatures, 20–80°K) for energy differences in Ge compared with values derived from local and nonlocal pseudopotentials. Some of the interband optical energies are shifted slightly to correct for displacement of peak energy critical points away from symmetry points; such corrected values are indicated by "~" and the procedure for making the corrections is discussed, e.g., in Ref. 9, or by D. Brust, Phys. Rev. 134, A1337 (1964). Semiempirical local-pseudopotential values, column 1; experimental values, column 2; values from our nonlocal potential, column 3. The equivalent local pseudopotential values, column 4; shifts in these values caused by s and d nonlocal terms, columns 5 and 6.

	CB[a]	Exper.	E_{nonl}	$E_{\mathrm{loc}}^{\mathrm{equiv}}$	ΔE_s	ΔE_d
$\Gamma_{1v} \to \Gamma_{25'}$	12.0	12.6±0.3[b]	12.49	11.44	0.002	1.05
$L_{2'v} \to \Gamma_{25'}$	9.9	10.6±0.4[b]	10.35	9.41	0.003	0.94
$L_{1v} \to \Gamma_{25'}$	6.9	7.7±0.2[b]	7.51	6.50	0.001	0.98
$\Sigma_{1\mathrm{min}} \to \Gamma_{25'}$	3.8	4.5±0.2[b]	4.55	3.66	0.000	0.89
$L_{3'v} \to \Gamma_{25'}$	1.1	1.4±0.2[c]	1.41	1.01	0.001	0.40
$\Gamma_{25'} \to \Gamma_{2'}$ (E_0)	1.2	0.98[e]	0.99	2.78	-0.006	-1.79
$\Gamma_{25'} \to \Gamma_{15}$ (E_0')	3.5	3.24[f]	3.25	3.87	-0.002	-0.62
$\Gamma_{25'} \to L_{1c}$	0.9	0.76[d]	0.77	1.91	-0.001	-1.14
$\Gamma_{25'} \to X_{1c}$	1.2	0.96[d]	1.02	1.74	0.000	-0.72
$L_{3'v} \to L_{1c}$ $(\sim E_1)$	2.0	2.2[e]	2.18	2.92	-0.002	-0.74
$L_{3'v} \to L_{3c}$ $(\sim E_1')$	5.4	5.8[g]	5.70	5.62	0.001	0.08
$X_{4v} \to X_{1c}$ $(\sim E_2)$	3.8	4.1[d,g]	4.17	4.17	0.001	0.00
$\Gamma_{25'} \to L_{3c}$	4.3	4.3[c]	4.29	4.60	0.003	-0.32

[a] Ref. 5.
[b] Ref. 4.
[c] Ref. 8.
[d] Ref. 9.
[e] Ref. 10.
[f] Ref. 11.
[g] Ref. 12.

about from the use of two additional nonlocal parameters. However, the energy shifts ΔE_s and ΔE_d shown in the last two columns indicate that all of the improvement has come from the d term; the s shifts ΔE_s are negligible and, in fact, we can set $a_0 = 0$ without sacrificing agreement between E_{nonl} and the experimental values. Thus all of the improved agreement shown in Table II has come about through the introduction of only one additional parameter.

The great advantage of the empirical pseudopotential method over conventional *ab initio* methods of calculation is that it does not require the determination of an accurate, self-consistent one-electron potential including the effects of exchange and correlation. For this reason it is interesting to compare ΔE_d in Table II with the discrepancies encountered in *ab initio* calculations. The largest shift, both absolutely and in percentage terms, is that of E_0, and it is $+1.8$ eV in Ge. The favorite tetrahedrally coordinated crystals for *ab initio* calculations are diamond and Si. In a recent *ab initio* calculation[13] for Si, the value obtained for E_0 was 2.75 eV, which can be compared with the experimental value[14] of 4.21 eV. This is a shift of $+1.5$ eV in the simpler case of Si. Note that an old local-pseudopotential calculation[15] for Si gave $E_0 = 4.2$ eV.

The results of these calculations suggest that it may be possible to achieve significantly better agreement with experiment through the use of one additional parameter (a_2) in pseudopotential calculations. By so doing one may hope to obtain more accurate values of V_{loc}^G, and thereby reproduce chemical trends in partially ionic compounds more accurately than has hitherto been the case.[16]

*Resident visitor from Department of Physics, Columbia University, New York, N. Y. 10027.

[1] M. L. Cohen and V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 37.

[2] F. Herman *et al.*, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1968), Vol. 8, p. 193.

[3] V. Heine and D. Weaire, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 249.

[4] W. D. Grobman and D. E. Eastman, Phys. Rev. Lett. 29, 1508 (1972). Similar data with slightly inferior resolution have been reported by L. Ley *et al.*, Phys. Rev. Lett. 29, 1088 (1972).

[5] M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

[6] V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 1.

[7] A. O. E. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965).

[8] W. E. Spicer and R. C. Eden, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow, 1968* (Nauka, Leningrad, U.S.S.R., 1968), Vol. 1, p. 61.

[9] F. Herman, R. L. Kortum, D. C. Kuglin, and R. A. Short, in *Quantum Theory of Atoms, Molecules, and the Solid State,* edited by P. O. Löwdin (Academic, New York, 1966).

[10] T. Nishino and Y. Hamakawa, J. Phys. Soc. Jap. 26, 403 (1969).

[11] D. E. Aspnes, Phys. Rev. Lett. 28, 913 (1972).

[12] R. R. Z. Zucca and Y. R. Shen, Phys. Rev. B 1, 2669 (1970); D. E. Aspnes, private communication.

[13] D. J. Stukel, Phys. Rev. B 3, 3347 (1971).

[14] D. E. Aspnes and A. A. Studna, Solid State Commun. 11, 1375 (1972).

[15] L. R. Saravia and D. Brust, Phys. Rev. 171, 916 (1968).

[16] J. A. Van Vechten, Phys. Rev. 187, 1007 (1969).

Excitonic Polarons in Molecular Solids*

Robert A. Bari
Brookhaven National Laboratory, Upton, New York 11973

(Received 1 February 1973)

The hard-core property of the Frenkel exciton is explicitly taken into account in the interaction of conduction electrons with a polarizable medium. The excitonic polaron bandwidth is less narrowed than in the boson approximation, does not vanish for infinite coupling, and is temperature independent. One consequence is that at high temperature the polaron motion is not dominated by hopping, but still contains a contribution from band motion.

The properties of quasi-one-dimensional electronic systems[1] have been of considerable interest in recent years. A recent paper of Chaikin, Garito, and Heeger[2] underscores the importance of understanding excitonic polaron effects in molecular crystals[3] with the electronic-chain plus