

## New Foundation for the Use of Pseudopotentials in Metals\*

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A theoretical foundation for the pseudopotential concept has been provided by switching from the Hartree-Fock framework to the  $G1$  framework. The new method allows *ab initio* determinations of the potential and removes many of the serious theoretical difficulties which have plagued the pseudopotential approach. The potential from *ab initio* calculations on the Li atom using the new approach is reported, along with the Fourier transform of the potential. There are still practical difficulties in solving the equations for the pseudopotentials of large atoms.

### INTRODUCTION

THE concept of the pseudopotential<sup>1</sup> has in recent years been extremely useful in developing the theory of metals.<sup>2-5</sup> Essentially the idea is to replace the Hartree-Fock equation for the valence orbitals

$$\begin{aligned} H^{\text{HF}}\phi_i &= \epsilon_i\phi_i, \\ H^{\text{HF}} &= T + V^{\text{HF}} \end{aligned} \quad (1)$$

(where  $T = -\frac{1}{2}\nabla^2$  is the kinetic term and  $V^{\text{HF}}$  is the potential term) by another equation

$$H_{\text{ps}}\phi_i^{\text{ps}} = \epsilon_i\phi_i^{\text{ps}}, \quad (2)$$

where  $\phi_i^{\text{ps}}$  is a "smooth" function without the nodes of  $\phi_i$ . In addition we take

$$H_{\text{ps}} = H^{\text{HF}} + V_R,$$

where  $V_R$  is a repulsive pseudopotential which cancels much of the negative  $V^{\text{HF}}$  in the core region of the atom. Since  $\phi^{\text{ps}}$  is smooth it can be well described with just a few plane waves, and since

$$V_{\text{eff}} = V^{\text{HF}} + V_R$$

is a weak potential, we can hope to use perturbation theory to describe scattering due to lattice vibrations, impurities, etc.<sup>4</sup> The net result is a quite aesthetic theory encompassing many of the interesting aspects of metals<sup>6</sup> and relevant even for discussing liquid metals<sup>7</sup> and the interactions leading to superconductivity.<sup>6,8</sup>

However, there are some well-known flaws in the pseudopotential theory. First, the pseudopotential is not unique<sup>3</sup>; there are an infinite number of different  $V_R$ , each of which leads to a different  $\phi^{\text{ps}}$ , but with the same  $\epsilon_i$ . Second, the new Hamiltonian is not Hermitian,<sup>5,9</sup> which leads to complications when considering scattering. Third, the  $V_R$  is an integral operator; it is not a local potential<sup>4</sup> even when  $V^{\text{HF}}$  is assumed to be local. This causes problems when considering scattering since the scattering matrix element between plane waves  $\mathbf{k}$  and  $\mathbf{k}+\mathbf{q}$ ,  $\langle \mathbf{k}+\mathbf{q} | V | \mathbf{k} \rangle$ , depends not only on  $\mathbf{q}$  but also on  $\mathbf{k}$ .<sup>5</sup>

These difficulties also lead to certain conceptual problems. It is clear that a solution to (1) can be interpreted as the eigenstate of an electron moving in the average field of the other electrons.<sup>10</sup> However, it is not at all clear that the solutions of (2) can be so interpreted. This is especially apparent since there are an infinite number of different equations like (2), each

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<sup>1</sup> H. Hellmann, *J. Chem. Phys.* **3**, 61 (1935); H. Hellmann and W. Kassatotschkin, *ibid.* **4**, 325 (1936).

<sup>2</sup> J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959); **116**, 880 (1959).

<sup>3</sup> M. H. Cohen and V. Heine, *Phys. Rev.* **125**, 1821 (1961).

<sup>4</sup> J. M. Ziman, *Advan. Phys.* **13**, 89 (1964).

<sup>5</sup> W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

<sup>6</sup> L. J. Sham and J. M. Ziman, *Solid State Phys.* **15**, 221 (1963).

<sup>7</sup> J. M. Ziman, *Phil. Mag.* **6**, 1013 (1960); C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, *Phil. Mag.* **7**, 865 (1962).

<sup>8</sup> V. Heine, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (John Wiley & Sons, Inc., New York, 1966), p. 16.

<sup>9</sup> B. J. Austin, V. Heine, and L. J. Sham, *Phys. Rev.* **127**, 276 (1962).

<sup>10</sup> W. A. Goddard, III, *Phys. Rev.* **157**, 81 (1967).

with a different  $\phi^p$ . In addition, since  $H_{pa}$  is not Hermitian, it would seem inappropriate to allege that it represents the Hamiltonian for an electron moving in the average field of the other electrons.

We have formulated a different approach<sup>10</sup> to electronic wave functions which very naturally leads to potentials and orbitals with the properties desired in the pseudopotentials and pseudo-orbitals but without the above-mentioned attendant difficulties.

### G1 METHOD AND PSEUDOPOTENTIALS

The new method, called the *G1* method,<sup>10,11</sup> is related to the Hartree-Fock method in that the variational principle is used to functionally optimize a general expression for the electronic wave function in which there is one orbital for each electron. However, in addition to satisfying the Pauli principle (accomplished in the Hartree-Fock method by the antisymmetrizer), the *G1* wave function is an eigenfunction of total spin for any choice of the  $N$  spatial orbitals (the Hartree-Fock method forces the spatial parts of the core orbitals to be identical in pairs in order to obtain the proper spin symmetry). The result is a set of equations

$$H_1\phi_1 = \epsilon_1\phi_1, H_2\phi_2 = \epsilon_2\phi_2, \dots, H_N\phi_N = \epsilon_N\phi_N, \quad (3)$$

determining the optimum orbitals. Here  $H_i$  has the form

$$H_i = T + V_{\text{nucel}} + U_i^{G1} = T + V_i^{G1},$$

where  $T = -\frac{1}{2}\nabla^2$ ,  $V_{\text{nucel}}$  is the potential due to the nuclei, and  $U_i^{G1}$  involves integrals over the other  $N-1$  orbitals (excluding  $\phi_i$ ) and can be considered as the average potential due to the other  $N-1$  electrons as seen by  $\phi_i$ . Thus, just as in the Hartree-Fock method,  $H_i$  can be interpreted as the Hamiltonian for an electron moving

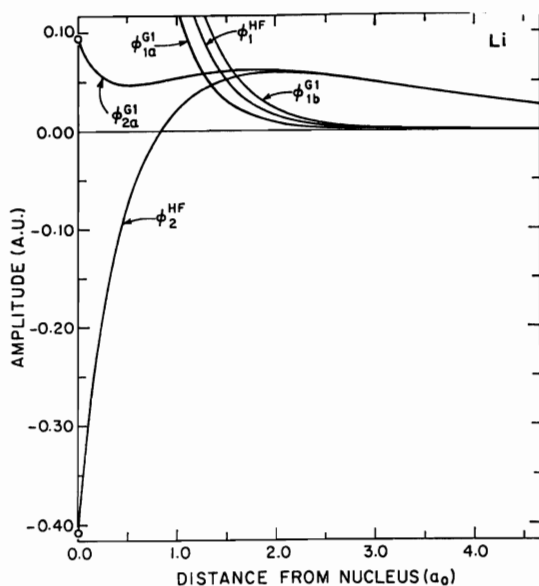


FIG. 1. The *G1* and Hartree-Fock valence orbitals for Li. Also shown are portions of the core orbitals.

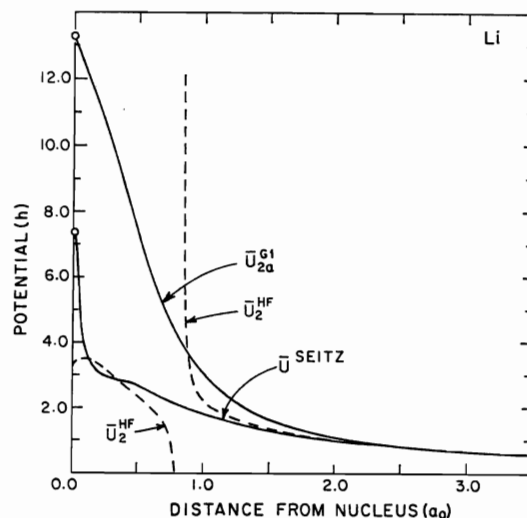


FIG. 2. The local potentials for the valence electron as obtained from the *G1* and Hartree-Fock methods and empirically (Seitz).  $\bar{U}$  is the local potential due to the core electrons. (Energies are in reduced atomic units for Li,  $1/h_{Li} = 27.208$  eV.)

in the average field of the other electrons. Hence we may interpret the many-electron wave function in terms of the one-electron orbitals  $\phi_i$  as if there were an electron in each orbital moving in the average field of the other electrons.

The  $H_i$  is Hermitian and is nonlocal (the  $U_i$  being an integral operator just as in the Hartree-Fock case). However, in contradistinction to the Hartree-Fock case, the orbitals  $\phi_i$  in (3) cannot be taken as orthogonal and the various  $H_i$  are not equivalent. That is, there is nothing in the *G1* many-electron wave function (as there is in the Hartree-Fock case) which forces the orbitals to be orthogonal (to orthogonalize the *G1* orbitals would, in general, raise the total energy quite significantly). Now it is just the orthogonality condition between Hartree-Fock orbitals which leads to the difficulties that led to the development of the pseudopotential formalism. Specifically, the orthogonality condition causes the valence orbitals to have nodes in the core region and thus implies that the effective potentials for these valence orbitals are strongly negative there. Hence the valence orbitals fluctuate drastically in the core region, requiring many plane waves in a plane-wave expansion, and the potential is too strong to allow a treatment of scattering in the Born approximation.<sup>4</sup> On the other hand, the *G1* valence orbital for the atom turns out to be nodeless and smooth in the core region, and the total atomic energy is far lower than the Hartree-Fock total energy.

In order to be specific, we shall discuss the case of the Li atom in the following since accurate *ab initio* atomic calculations have already been carried out<sup>11</sup> and since Li is a prototype for the systems of interest. Each of the *G1* orbitals is the lowest solution for its respective

<sup>11</sup> W. A. Goddard, III, Phys. Rev. 169, 120 (1968).

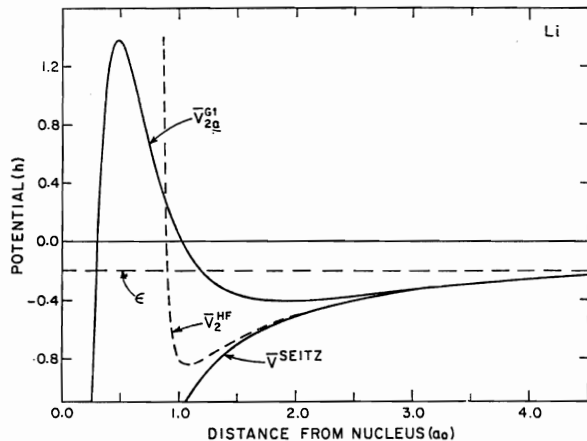


FIG. 3. The effective potentials for the valence electron as obtained from the  $G1$  and Hartree-Fock methods and empirically (Seitz).  $\bar{U}$  is the local potential due to the core electrons and  $\bar{V}$  is the total potential,  $\bar{V} = \bar{U} - 3/r$ . (Energies are in reduced atomic units for Li,  $1\hbar_{Li} = 27.208$  eV.) On the inner side of the node of the Hartree-Fock orbital, the  $\bar{V}^{HF}$  is negative.

Hamiltonian and each is nodeless. Two orbitals,  $\phi_{1a}$  and  $\phi_{1b}$ , are concentrated in the core region and the other, the valence orbital  $\phi_{2a}$  is smooth and large out to about  $5a_0$ . In Fig. 1 we compare the  $G1$  and Hartree-Fock orbitals for Li. Since the  $G1$  orbitals are nodeless, it is straightforward to solve the equation

$$H_i' \phi_i = [-\frac{1}{2} \nabla^2 - Z/r + \bar{U}_i(r)] \phi_i(r) = \epsilon_i \phi_i(r) \quad (4)$$

for a local potential  $\bar{U}_i(r)$  such that the local operator  $H_i'$  has the same solution,  $\phi_i$  and  $\epsilon_i$ , as the nonlocal operator  $H_i$  in (3); i.e.,

$$\bar{U}_i(r) = \epsilon_i + \frac{Z}{r} \frac{l(l+1)}{2r^2} + \frac{\theta_i''(r)}{2\theta_i(r)}, \quad (5)$$

where  $\theta(r) = r\phi(r)$  and  $\theta'' = d^2\theta/dr^2$ . The  $\bar{U}_{2a}$  for the valence electron of Li is shown in Fig. 2 and the total effective potential

$$\bar{V}_{2a} = \bar{U}_{2a} - Z/r \quad (6)$$

is shown in Fig. 3. Also shown in Figs. 2 and 3 are the potentials for the Hartree-Fock valence orbital<sup>12</sup> and the potentials for a commonly used empirical potential for Li, the Seitz potential.<sup>13</sup> [In the Hartree-Fock method the valence orbital  $\theta_2$  has a node and thus the

<sup>12</sup> A. W. Weiss, *Astrophys. J.* 138, 1262 (1963). We use the Weiss Hartree-Fock wave function for Li because the orbitals satisfy the cusp conditions exactly (if the orbital does not satisfy the cusp condition at the nucleus, the  $\bar{U}_i$  is infinite there). Since the Hartree-Fock valence orbital for Li has a node, straightforward application of (5) leads to erratic behavior in the region of the node.

<sup>13</sup> F. Seitz, *Phys. Rev.* 47, 400 (1935). The published table for the potential was in error and has been corrected by W. Kohn and N. Rostoker, *Phys. Rev.* 94, 1116 (1954); however, it would appear that one of their values is in error. Specifically for the potential to be smooth, the value of  $-r\bar{V}$  at  $r=0.92$  should be about 2.466 rather than 2.4242.

TABLE I. Energies for several excited states of the Li atom calculated using the effective potential,  $\bar{V}_{2a}^{G1}$ , from Fig. 2. (Energies are in reduced atomic units for Li,  $1\hbar_{Li} = 27.208$  eV.)

	Calc.	Expt. <sup>a</sup>
2s	-0.19633	-0.19816
3s	-0.07475	-0.07419
4s	-0.03893	-0.03862
5s	-0.02381	-0.02364
6s	-0.01605	-0.01595
2p	-0.11233	-0.13025
3p	-0.05107	-0.05724
3d	-0.05533	-0.05561

<sup>a</sup> C. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), using  $1\hbar_{Li} = 219457.454$  cm<sup>-1</sup> [from C. W. Scherr, J. N. Silverman, and F. A. Matsen, *Phys. Rev.* 127, 830 (1962), Table V].

local potential defined by (5) has a singularity.<sup>14</sup>] Thus we see that the  $G1$  effective potential is rather weak. In fact, from Figs. 1-3 we see that the  $G1$  orbital and  $G1$  local potential for the valence state of Li have exactly the forms postulated for the pseudo-wave-function<sup>2</sup> and pseudopotential.<sup>8</sup> However,  $\bar{V}_{2a}^{G1}$  is unique, Hermitian, and local, and the  $\phi_{2a}^{G1}$  is the eigenstate of the one-electron Hamiltonian obtained directly from the variational principle. Thus, conceptually everything is in order and all the problems mentioned in the Introduction have been removed. By replacing the Hartree-Fock method by the  $G1$  method we have very naturally obtained a firm foundation for all of the concepts of the pseudopotentials, ingeniously developed over the last few years, avoiding, however, most of the attendant difficulties. We see that these concepts are much more fundamental than has been previously supposed.<sup>15</sup> In the  $G1$  and pseudopotential methods the weakly bound orbital is described as the lowest (hence nodeless) state of a weak potential, whereas this orbital is described in the Hartree-Fock method as a higher (node containing) state of a deep or strong potential.

There is, however, one thing left to clear up. If the local potential  $\bar{U}(r)$  in (5) really represents an average potential due to the core electrons, then the excited states in this potential should correspond approximately with the actual excited states of the atom. In Table I we compare the experimental energies for the  $n^2S$  states with  $n$  up to 6 to those calculated using the

<sup>14</sup> Note that  $\theta_i''$  of (5) does not in general have a node at the node of  $\theta_i$ . For example, for Li the Hartree-Fock equations become

$$-\frac{1}{2}\theta_2''(1) - \frac{Z}{r}\theta_2(1) + 2\left(\int d\mathbf{x}_2 \frac{\theta_1^*(2)\theta_1(2)}{r_{12}}\right)\theta_2(1) - \left(\int d\mathbf{x}_2 \frac{\theta_1^*(2)\theta_2(2)}{r_{12}}\right)\theta_1 = \epsilon_{22}\theta_2(1) + \epsilon_{21}\theta_1(1).$$

Thus at the node of  $\theta_2$  we have

$$\frac{1}{2}\theta_2''(1) = -\left(\epsilon_{21} + \int d\mathbf{x}_2 \frac{\theta_1^*(2)\theta_2(2)}{r_{12}}\right)\theta_1(1),$$

which need not be zero (here  $\epsilon_{21} = \langle \theta_2 | 1/r_{12} | \theta_2 \rangle$ ). I thank Professor R. M. Pitzer for a discussion on this point.

<sup>15</sup> B. J. Austin and V. Heine, *J. Chem. Phys.* 45, 928 (1966).

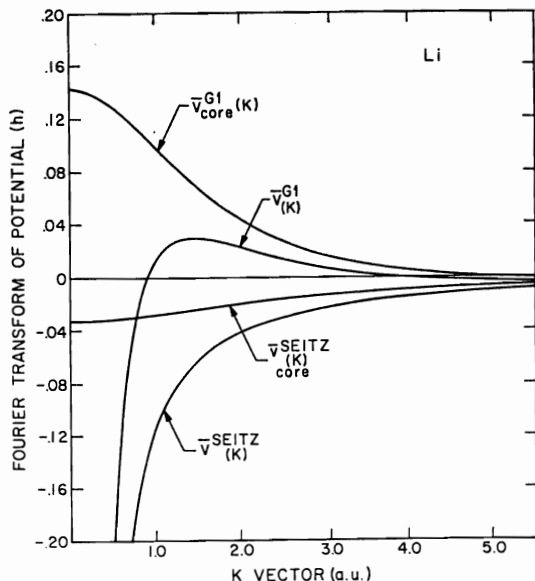


FIG. 4. The Fourier transforms of the core potential,  $\bar{V}_{\text{core}} = \bar{U} - 2/r$  and the total effective potential,  $\bar{V} = \bar{U} - 3/r$ . See Ref. 18 for a precise definition of the Fourier transform.

$\bar{U}_{2a}(\mathbf{r})$  obtained from the  $2s$  orbital,  $\phi_{2a}^{G1}$ .<sup>16</sup> We see that the calculated energies for the  $ns^2S$  states are within about 1% of the experimental values, and thus as far as  $s$  states are concerned the local potential does seem to be equivalent to the nonlocal potential it replaces. This does not extend, however, to states of different symmetry. A portion of the exchange term in the nonlocal  $\bar{U}_{2a}^{G1}$  depends directly on the overlap between core and valence orbitals which is significantly changed when the valence orbital has a different symmetry. A similar

<sup>16</sup> Thus the calculated excitation energies are based on the assumption that the core orbitals are the same for all excited states. Of course they do rearrange some. If the rearrangement were large it would make less sense to assume that the core electrons can be replaced by the same potential for all states. The effect of the rearrangement on the calculated ionization energy is small, however, and should be about  $0.00003h$ ; see P. C. Chow and L. Kleinman, Phys. Rev. **162**, 105 (1967).

difficulty occurs in the pseudopotential approach, where there is a different pseudopotential for each symmetry.<sup>2-5,17</sup>

Now that we at last have pseudopotentials, derived from *ab initio* calculations, there are many areas for possible applications.<sup>4</sup> Since many applications, for example, calculations of band structure and electron-phonon interactions, require the Fourier transform of the potential,<sup>4</sup> we show in Fig. 4 the Fourier transform,<sup>18</sup>  $\bar{v}_{\text{core}}^{G1}(\mathbf{k})$ , of  $\bar{V}_{\text{core}}^{G1}(\mathbf{r}) \equiv \bar{U}_{2a}^{G1}(\mathbf{r}) - 2/r$ .  $\bar{V}_{\text{core}}^{G1}$  is the net core potential to which we must add  $-1/r$  in the case of the atom and, in the case of a metal, also some sort of shielded potential due to the other atoms. The Fourier transform  $\bar{v}_{2a}^{G1}(\mathbf{k})$  of  $\bar{V}_{2a}^{G1}(\mathbf{r})$  is also included. For comparison purposes the Fourier transform of the Seitz core potential is also given in Fig. 4. Thus we see that the weakness of the  $G1$  potential does indeed lead to much smaller Fourier coefficients. Note that since  $\bar{V}_{2a}^{G1}(\mathbf{r})$  is local, the matrix element between plane waves  $\mathbf{k}$  and  $\mathbf{k} + \mathbf{q}$  is just the Fourier transform of  $\bar{V}$ ,

$$\langle \mathbf{k} + \mathbf{q} | \bar{V} | \mathbf{k} \rangle = \bar{v}(\mathbf{q}).$$

The major difficulty with the  $G1$  approach is that the initial solution of Eqs. (3) for the atoms is much more complex than in the Hartree-Fock case. Calculations have at the present time been carried out only for He, Li, and Be (and isoelectronic ions). We are in the process of developing programs for atoms up through Na.

#### ACKNOWLEDGMENT

The author thanks Len Doberne for assistance in some of the calculations.

<sup>17</sup> J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, London, 1965).

<sup>18</sup> We define  $\bar{v}(\mathbf{k}) = (1/\Omega) \int e^{i\mathbf{k}\cdot\mathbf{r}} \bar{V}(\mathbf{r}) d^3\mathbf{r}$ , where  $\Omega$  is taken to be the volume per atom in Li metal. We used  $\Omega = \frac{1}{2}a^3 = 142.12068 a_0^3$  which is based on  $a = 6.575a_0 = 3.479\text{\AA} = 3.472\text{\AA}$  at  $4^\circ\text{K}$  [W. Pearson, Can. J. Phys. **32**, 708 (1954), using conversion constants from E. R. Cohen and J. M. W. Dumond, Rev. Mod. Phys. **37**, 537 (1965)].