Kohn-Sham exchange potential exact to first order in $\rho(\mathbf{K})/\rho_0$

P. R. Antoniewicz and Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712
(Received 9 January 1985)

The Kohn-Sham exchange potential may be written, exact to first order in $\rho(\mathbf{K})/\rho_0$, $V_x^{\mathrm{KS}}=-\frac{3}{2}(3/\pi)^{1/3}\rho_0^{-2/3}\sum_{\mathbf{K}}'\rho(\mathbf{K})F(K)e^{i\mathbf{K}\cdot\mathbf{r}}$. Here we evaluate the universal function $F(K/k_F)$ for all K/k_F and find large corrections to the local-density approximation which should result in much improved values for semiconductor energy gaps.

We have recently[1] shown that the Kohn-Sham (KS)[2] exchange potential may be written exactly to first order in $\rho(\mathbf{K})/\rho_0$;

$$V_x^{\mathrm{KS}}=-\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3}\rho_0^{-2/3}\sum_{\mathbf{K}}'\rho(\mathbf{K})F(K)e^{i\mathbf{K}\cdot\mathbf{r}}\ , \tag{1}$$

where $V_x^{\mathrm{KS}}=\delta E_x/\delta\rho(\mathbf{K})$ and E_x is defined to be the Fock energy of the eigenfunctions of the self-consistent density functional potential which differs only negligibly from the Hartree-Fock exchange energy. $F(K)$ contains an integral and was evaluated in two limits:

$$F(K\to\infty)=\frac{8}{27}\frac{k_F^2}{K^2},\quad \mathbf{F}(\mathbf{K}\to 0)=\frac{2}{9}+\frac{2}{81}\frac{K^2}{k_F^2}\ .$$

The $\frac{2}{9}$ in the $K\to 0$ limit is just the local density approximation (LDA) and the

$$\frac{2}{81}\frac{K^2}{k_F^2}$$

corresponds to a gradient term larger than that obtained by Sham[3] by a factor of $\frac{8}{7}$. We showed that this discrepancy arises because the $\lambda\to 0$ limit of screened exchange used by Sham is not identical to unscreened exchange. In this Brief Report we evaluate $F(K)$ numerically for all K. That such an exact universal curve exists and can be calculated is interesting in and of itself. That it shows large deviations from the LDA has important considerations for energy-band calculations. For the (111), (200), and (220) Fourier coefficients of potential which determine the energy gaps in diamond and zinc-blende semiconductors, the magnitude of the exchange potential is increased. This tends to increase energy gaps so that it is quite likely that density functional theory yields energy gaps in much better agreement with experiment than heretofore believed, due to the inadequacy of the LDA.

Because of the singular nature of this integral (whence arose the gradient-expansion controversy), we deem it useful to outline our evaluation procedure. From Eqs. (5), (12), and (18) of Ref. 1,

$$F(K)=-A(K)I(K)\ , \tag{2}$$

where

$$I(K)=\int d^3k\,d^3k'|\mathbf{k}-\mathbf{k}'|^{-2}\left(1-\frac{1}{2}\frac{K^2+2\mathbf{k}'\cdot\mathbf{K}}{K^2+2\mathbf{k}\cdot\mathbf{K}}-\frac{1}{2}\frac{K^2+2\mathbf{k}\cdot\mathbf{K}}{K^2+2\mathbf{k}'\cdot\mathbf{K}}\right)\frac{f(\mathbf{k}+\mathbf{K})-f(\mathbf{k})}{\frac{1}{2}K^2+\mathbf{k}\cdot\mathbf{K}}\frac{f(\mathbf{k}'+\mathbf{K})-f(\mathbf{k}')}{\frac{1}{2}K^2+\mathbf{k}'\cdot\mathbf{K}}\ , \tag{3}$$

$$A(K)=\frac{4}{9\pi^2}\left[2+\left(\frac{2k_F}{K}-\frac{K}{2k_F}\right)\ln\left|\frac{2k_F+K}{2k_F-K}\right|\right]^{-2}\ , \tag{4}$$

and $f(\mathbf{k})$ is the Fermi function. A little manipulation yields

$$I(K)=\int\left(\frac{[(\mathbf{k}+\mathbf{k}')\cdot\mathbf{K}]^2}{|\mathbf{k}+\mathbf{k}'|^2}-\frac{[(\mathbf{k}-\mathbf{k}')\cdot\mathbf{K}]^2}{|\mathbf{k}-\mathbf{k}'|^2}\right)\frac{f(\mathbf{k}-\frac{1}{2}\mathbf{K})f(\mathbf{k}'-\frac{1}{2}\mathbf{K})}{(\mathbf{k}\cdot\mathbf{K})^2(\mathbf{k}'\cdot\mathbf{K})^2}d^3kd^3k'\ . \tag{5}$$

Choosing cylindrical cordinates ($d^3k=\frac{1}{2}d\theta dk_\perp^2dk_z$) results in integrals of the form

$$\int_0^{2\pi}\frac{(k_z'\pm k_z)^2d\theta d\theta'}{(k_z'\pm k_z)^2+k_\perp^2+k_\perp'^2-2k_\perp k_\perp'\cos\theta}\ ,$$

which are easily evaluated to yield

$$\begin{aligned}I(K)=(\pi/K)^2\int\{&(k_z+k_z')^2[(k_\perp^2-k_\perp'^2)^2+2(k_z+k_z')^2(k_\perp^2+k_\perp'^2)+(k_z+k_z')^4]^{-1/2}\\&-(k_z'-k_z)^2[(k_\perp^2-k_\perp'^2)^2+2(k_z-k_z')^2(k_\perp^2+k_\perp'^2)+(k_z-k_z')^4]^{-1/2}\}\\&\times f(\mathbf{k}-\tfrac{1}{2}\mathbf{K})f(\mathbf{k}'-\tfrac{1}{2}\mathbf{K})k_z^{-2}k_z'^{-2}dk_\perp^2dk_\perp'^2dk_zdk_z'\ .\end{aligned} \tag{6}$$

Letting $z=k_z-\frac{1}{2}K$, $z'=k_z'-\frac{1}{2}K$, and integrating over $k_\perp^2+k_\perp'^2$ and $k_\perp^2-k_\perp'^2$ between the limits $0<k_\perp^2<k_F^2-z^2$ and

$0 < k_\perp'^2 < k_F^2 - z'^2$, one obtains after some effort

$$I(K) = (\pi/K)^2 \int_{-k_F}^{k_F} dz \int_{-z}^{z} dz' (z + \tfrac{1}{2}K)^{-2} (z' + \tfrac{1}{2}K)^{-2} \times \sum_{i=1}^{2} (-1)^i a_i \{ b_i - a_i + z^2 + z'^2 - 2k_F^2 + 2(k_F^2 - z^2) \ln[(z^2 - z'^2 + a_i + b_i)/2a_i] + 2(k_F^2 - z'^2) \ln[2(k_F^2 - z'^2)/(z^2 - z'^2 - a_i + b_i)] \} , \quad (7)$$

where

$$a_1 = (z - z')^2, \quad a_2 (z' + z + K)^2 \quad (8)$$

and

$$b_i = [(a_i + 2k_F^2 - z^2 - z'^2)^2 - 4(k_F^2 - z^2)(k_F^2 - z'^2)]^{1/2} . \quad (9)$$

We have evaluated Eq. (7) numerically, normalizing to $k_F = 1$. Note when either z or $z' = -\frac{1}{2}K$ that $a_1 = a_2$ so that the apparent second-order singularities are actually first order. To obtain the principal value of the integral we evaluated the integrand at mesh points z_n and $z_n' = \pm n/1000$ with n odd and required that $\frac{1}{2}K = m/1000$ with m even.

In Fig. 1 we plot the universal curve $F(\kappa = K/k_F)$ for $\kappa \leq 4$; in the inset we show $dF/d\kappa$ around $\kappa = 2$ where $dF/d\kappa$ appears to become infinite. For $\kappa > 4$ see Fig. 2, where $F(\kappa)$ divided by its limiting value $8/27\kappa^2$ is plotted against κ^{-1} for $4 \leq \kappa \leq \infty$. In Fig. 3 we plot $F(\kappa) - \frac{2}{9}$ divided by the $\kappa \to 0$ limiting value we previously obtained,[1] $2\kappa^2/81$, for $0.004 \leq \kappa \leq 0.25$. Note that as $\kappa \to 0$ the calculation becomes numerically unstable because of both the $1/\kappa^2$ in the ratio and the $1/\kappa^2$ in $I(\kappa)$. There is a huge amount of cancellation within the integral $I(\kappa)$ that occurs on a scale of order κ so that the mesh used in the numerical integration must be small compared to κ. Besides our standard 1000-point mesh with $\Delta z/k_F = \Delta z'/k_F = 0.002$, we used meshes twice and four times as fine. We also used Control Data Corporation (CDC) double precision (25 significant figures) here.[4] Each κ point with double precision and 4000-point mesh required 1 h of CDC Cyber time. The ratio takes the value 1.250 at $\kappa = 0.12$ and slowly increases as κ increases. Observing the three curves, it appears that if an infinitely fine mesh and infinite number of significant figures could be used in the calculation, the ratio would approach a value not much smaller than 1.24 as $\kappa \to 0$ but that $\kappa = 0$ is an essential singularity where the ratio is undefined. Thus a unique value of γ_x, the gradient expansion coefficient, cannot be obtained by expanding about $\kappa = 0$ (explaining the discrepancy between the $\lambda \to 0$ screened exchange and unscreened exchange results) but may be obtained by extrapolating the curves in Fig. 3 back toward $\kappa = 0$. In spite of this we agree that γ_{Sham} is the correct γ_x to add to γ_{MB}, the Ma-Brueckner[5] correlation coefficient, to obtain γ_{xc} whose expansion is unique.[6]

We wish to emphasize that $V_{xc}(\mathbf{K}) = V_x(\mathbf{K}) + V_c(\mathbf{K})$, i.e., that although correlation screens exchange self-energy, it is merely additive to the KS exchange potential.[7] Making the small $\rho(\mathbf{K})/\rho_0$ expansion of the Hedin-Lundqvist[8] LDA correlation potential one obtains

$$V_c(\mathbf{K} \to \mathbf{0})/V_x(\mathbf{K} \to \mathbf{0}) = 1.609(1 + 21/r_s)^{-1} , \quad (10)$$

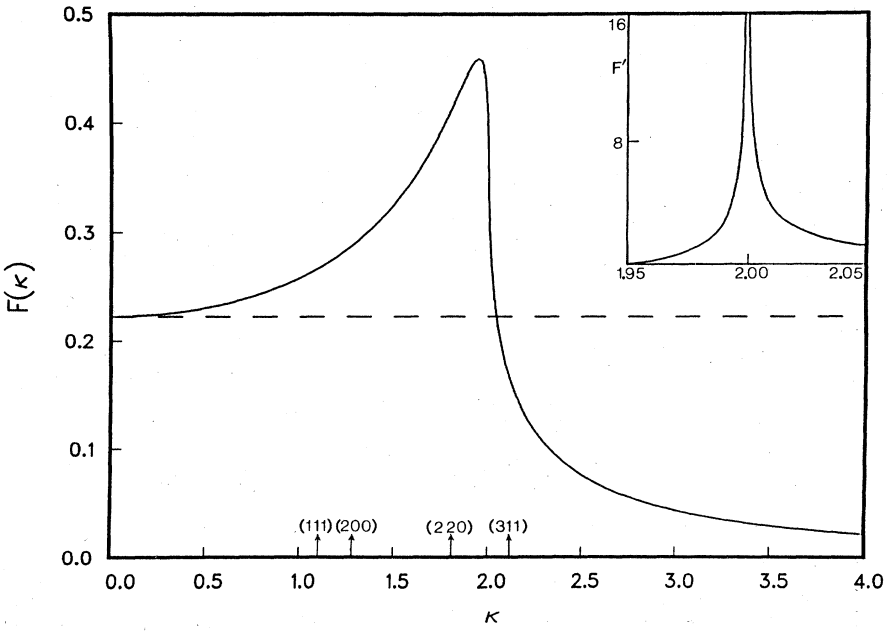

FIG. 1. The dimensionless quantity $F(\kappa)$ appearing in Eq. (1) vs $\kappa = K/k_F$. Values of κ equivalent to the (111), (200), (220), and (311) reciprocal-lattice vectors in zinc blende are indicated. The horizontal line is the LDA result $F(\kappa) = \frac{2}{9}$. The inset shows $dF/d\kappa$ in the region it becomes infinite.

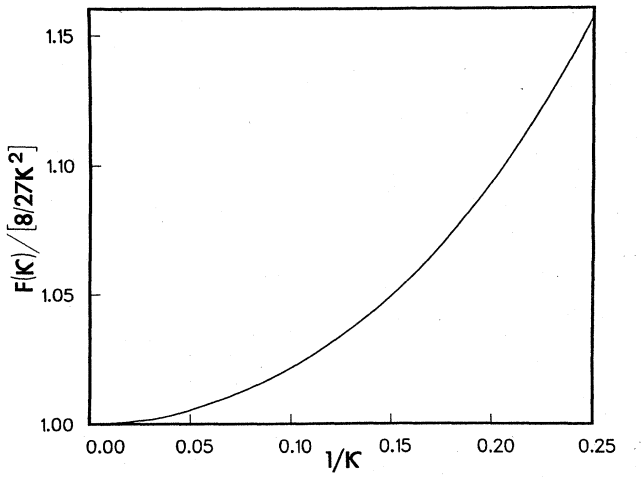

FIG. 2. The ratio of $F(\kappa)$ to $8/27\kappa^2$ plotted against $1/\kappa$ for $4 \leq \kappa \leq \infty$.

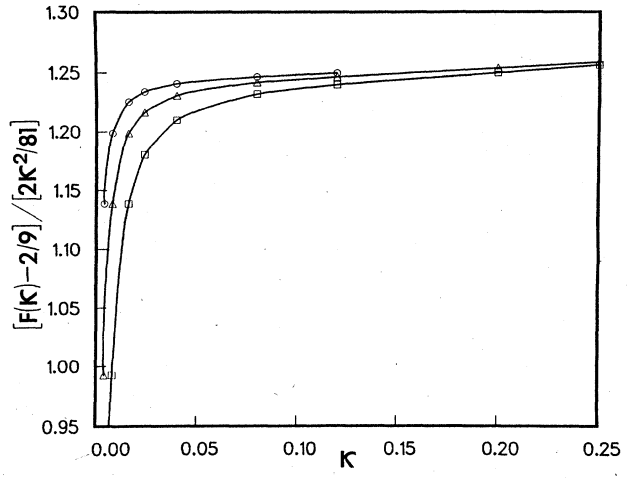

FIG. 3. The ratio of $[F(\kappa)-\frac{2}{9}]$ to $2\kappa^2/81$ for $0.004 \leq \kappa \leq 0.25$ calculated with 1000-point (□), 2000-point (Δ), and 4000-point (○) meshes.

where $r_s=(4\pi\rho_0/3)^{-1/3}$. For Si ($r_s=2$), $V_c(\mathbf{K}=0)$ is only 14% of $V_x(\mathbf{K}=0)$. Since γ_{MB} indicates $-V_c$ decreases for small $\mathbf{K}$ and it must vanish for $\mathbf{K}\rightarrow\infty$, we suspect it decreases monotonically and that the ratio V_c/V_x takes its maximum value at $\mathbf{K}=0$. Because a linear expansion in $\rho(\mathbf{K})/\rho_0$ is only marginal for semiconductors, we suggest that Eq. (1), with $F(K)$ replaced by $F(K)-\frac{2}{9}$ and with $\rho(\mathbf{K})$ the valence-charge density, be added as a correction to the LDA exchange potential. We note from Fig. 1 that this correction is about 20%, 30%, and 85% of the LDA exchange for the (111), (200), and (220) Fourier components. On the average this potential (especially with the inclusion of correlation) is similar to the Slater[9] potential for the important Fourier components. The Slater exchange potential, which is 50% larger than the KS for all Fourier components, is known to result in much better semiconductor energy gaps. Thus is explained our observation of many years ago[10] that Fock exchange results in Si band gaps about a factor of 3 too large but the Slater exchange potential or screened Fock exchange results in approximately correct gaps. The large errors in energy gaps obtained from KS eigenvalues (up to 83% too small[11]) have recently been attributed to[12,13] a discontinuity in $\delta E_{xc}/\delta\rho$ across the gap. We conclude here that a large part of that error is due to the use of the LDA and that the discontinuity in $\delta E_{xc}/\delta\rho$ is smaller than originally[12,13] suggested. Hybertsen and Louie,[14] using the weighted density approximation, have reached the same conclusion.

After this work was completed, it was brought to our attention that Sham[15,16] had published a curve essentially identical to Fig. 1. Sham calculated

$$\frac{F(\kappa)}{F(0)}=\frac{\chi_1(\kappa)/\chi_1(0)}{[\chi_0(\kappa)/\chi_0(0)]^2}\ , \tag{11}$$

where $\chi=\chi_0+\chi_1+\cdots$ is an expansion of the Hartree-Fock susceptibility in powers of e^2. We know of no proof that this first order in e^2, Hartree-Fock $F(\kappa)$, is identical to our $F(\kappa)$ calculated for Fock exchange of Kohn-Sham eigenfunctions. However, numerically they are almost so. A numerical listing of our $F(\kappa)$, accurate to four decimal places, is available from us. The Sham $F(\kappa)$, calculated from Geldart and Taylor's[17] values of $\chi_1(\kappa)$ and $\chi_0(\kappa)$, differs from ours by $\pm 0.2\%$ which is slightly larger than one would like to attribute to numerical error.[18] We also note that, even if the χ's of Ref. 17 are exact, they do not contain enough significant figures to obtain the ratio plotted in Fig. 3 of this paper.

One of us (P.A.) acknowledges support from the Department of Energy under Grant No. DE-FG05-84ER45064 and the other (L.K.) from the Robert A. Welch Foundation and the National Science Foundation under Grants No. DMR-80-19518 and No. DMR-84-12408.

[1]L. Kleinman, Phys. Rev. B **30**, 2223 (1984).
[2]W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965).
[3]L. J. Sham, in *Computational Methods in Band Theory,* edited by P. J. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York and London, 1971), p. 458.
[4]For the 1000-point mesh the difference between single and double precision becomes negligible for $\kappa > 0.016$ and for the 2000-point mesh for $\kappa > 0.024$.
[5]S.-K. Ma and K. A. Brueckner, Phys. Rev. **165**, 18 (1968).
[6]D. C. Langreth and J. P. Perdew, Phys. Rev. B **21**, 5469 (1980).
[7]This is because $V_x(\mathbf{K})=\delta E_x/\delta\rho(\mathbf{K})$ and the exchange ground-state energy is completely independent of correlation.
[8]L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).
[9]J. C. Slater, Phys. Rev. **81**, 385 (1951).
[10]J. C. Phillips and L. Kleinman, Phys. Rev. **128**, 2098 (1962).
[11]N. E. Christensen, Phys. Rev. B **30**, 5753 (1984).
[12]L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).
[13]J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).
[14]M. S. Hybertsen and S. G. Louie, Solid State Commun. **51**, 451 (1984).
[15]L. J. Sham, Phys. Rev. B **7**, 4357 (1973).
[16]See also F. Brosens, L. F. Lemmens, and J. T. Devreese, Phys. Status Solidi (b) **81**, 551 (1977).
[17]D. J. W. Geldart and R. Taylor, Can. J. Phys. **48**, 155 (1970).
[18]At $\kappa=2$, $\chi_0(\kappa)/\chi_0(0)\equiv\frac{1}{2}$ so that to obtain our value of $F(2)/F(0)\simeq 0.3643/0.2222$ requires $\chi_1(\kappa)/\chi_1(0)=0.4099$ rather than the 0.4089 of Ref. 17.