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Calculated shifts in electronic states for fcc hydrogen

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First-order shifts in electron energy levels at k_F and at high-symmetry points are calculated for hypothetical fcc hydrogen using a perturbation procedure in conjunction with the modified-plane-wave method. The shifts are calculated for hydrostatic, tetragonal, and trigonal strains. For hydrostatic compression the general trend is that levels $\lesssim E_F$ shift downward while levels $\gtrsim E_F$ shift upward; there is a general widening of the gap between first and second bands. For the shear cases the numerical results satisfy symmetry requirements where tested. For comparable strain parameter e the shifts at E_F under shear are considerably larger than in the hydrostatic case.

I. INTRODUCTION

There has been considerable interest recently in PdH (PdD) and Pd–noble-metal–H (Pd–noble-metal–D) systems because of their superconducting properties.[1-15] Electronic properties have been calculated for fcc H by Switendick,[16] for Pd by Andersen,[17] Mueller *et al.*,[18] and Watson-Yang *et al.*,[19] for the PdH system by several authors,[7-14] and for the Pd-Ag-H system by Papaconstantopoulos and Economou.[15] It is of interest to know how the electron energy levels most pertinent to superconductivity, those near the Fermi level (E_F), shift with pressure. In this paper, as a preliminary study, we look at electron energy-level shifts in (hypothetical) fcc hydrogen. (Metallic hydrogen is also of interest in its own right.) Similar calculations are planned for the PdH and Pd-Ag-H systems.

For the calculation of the unperturbed energy levels (E^0) we used the modified-plane-wave (MPW) method.[20-30] The energy shifts (ΔE) are calculated by a perturbation procedure.[24,25] (Both E^0 and ΔE for a given representation for a given $\vec{k}$ point are calculated at the same time.)

In Sec. II we make a preliminary calculation for E^0 and compare results with those of Switendick.[16] In Sec. III we give energy shifts at k_F (in the $\langle 001\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions) and at some high-symmetry points for hydrostatic (Γ_1), tetragonal (Γ_{12}), and trigonal ($\Gamma_{25'}$) strains. A brief summary is given in Sec. IV.

II. UNSTRAINED ENERGY LEVELS

A. Comparison of E^0 levels with Switendick; a preliminary calculation

As the existence of metallic hydrogen is not yet established the choice of lattice is somewhat arbitrary; we chose to use, as far as feasible, the parameters of Switendick's earlier calculation.[16] The lattice is fcc with lattice constant (a_0) of 4.196 56 a.u. This gives a Wigner-Seitz radius (r_{WS}) of 1.64 a.u. and a muffin-tin radius (r_{mt}) of 1.483 71 a.u. We use this r_{mt} for comparison purposes *only*; for the actual calculation (including perturbation) we reduce r_{mt} slightly.

The crystal potential is generated from the atomic hydrogen potential using the Mattheiss-Loucks superposition scheme[26,27] and Slater's free-electron exchange approximation.[28] (Switendick also used this procedure.) In our comparison of crystal potential we use the first six "rings" of neighboring atoms.[29,30] For hydrogen, the atomic wave function can be written analytically as $u(r)=2re^{-r}$, where $\psi(r)_{\text{atomic}}=[u(r)/r]f(\theta,\phi)$ and, for hydrogen, $f(\theta,\phi)=1$.

For comparison with Switendick[16] only, $\overline{V}$, the constant value of the potential in the region between muffin tins, is taken as his value of −1.354 Ry. Table I gives our (preliminary calculation) electron energy levels and those of Switendick for some high-symmetry points. For this table the trial expansion function includes the hydrogen 1s atomiclike function (when allowed by symmetry) and symmetrized plane waves up to $M^2 \equiv (a_0^2/4\pi^2) \times |\vec{k}+\vec{K}|^2$ of approximately 40 (except for K_1 and W_3 for which $M^2 \simeq 29$ and 35, respectively). The agreement for Γ_1, $X_{4'}$, L_1, and K_1 (upper) is excellent; other levels differ from Switendick's by amounts ranging from 0.01 to 0.04 Ry with our levels generally lying above Switendick's augmented-plane wave (APW) values.

B. Change in r_{mt} for computational convenience—recomputation of $\overline{V}$

In the calculation now described (the main calculation of this paper) we reduce r_{mt} slightly (2%)

TABLE I. Comparison of unperturbed energy levels (preliminary calculation) with Switendick.[a] $a_0 = 4.196\,56$ a.u., $r_{\mathrm{WS}} = 1.64$ a.u., $r_{\mathrm{mt}} = 1.483\,71$ a.u., and $\overline{V} = -1.354$ Ry (all identical to Switendick's values). Alternate columns give the irreducible representation and energy level in Ry. Switendick's values are taken from his Fig. 1 and are shifted by -1.354 Ry. The units for $\vec{k}$ are $2\pi/a_0$.

Symmetry point[b] $\vec{k}$	Γ $(0,0,0)$		X $(0,0,1)$		L $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$		K $(\frac{3}{4},\frac{3}{4},0)$		W $(1,0,\frac{1}{2})$	
This work			4′	0.618	2′	0.102	1	0.955	3	1.177
Switendick[a]			4′	0.612	2′	0.112	1	0.958	3	1.138
This work	1	−1.899	1	−0.041	1	−0.536	1	0.037	1	0.146
Switendick[a]	1	−1.897	1	−0.064	1	−0.539	1	0.020	1	0.122

[a] Reference 16.

[b] Reference 33.

from the half nearest-neighbor value. This allows for compression of the crystal without overlap or recalculation of the atomiclike functions.[31] The new r_{mt} is 1.454 03 a.u. Changing the muffin-tin radius leads to a new value for $\overline{V}$. Our procedure for computing this average V is that of Loucks[27]:

$$\overline{V} \equiv V_{\text{average}} \equiv \int_b^c V(r) r^2\, dr \Big/ \int_b^c r^2\, dr\,, \qquad (1)$$

with $b = r_{\mathrm{mt}}$ and $c = r_{\mathrm{WS}}$; $V(r)$ is the crystal potential determined using the Mattheiss-Loucks superposition prescription. Our $\overline{V}$ is $-1.396\,67$ Ry. We emphasize that we depart from Switendick's parameters in two ways: (i) $\overline{V}$ is calculated using a different procedure; (ii) r_{mt} is reduced by 2% causing a further change in $\overline{V}$. Various tests indicate that the first change has by far the larger effect.[32] Although we have calculated energy levels at a very small number of $\vec{k}$ points, these E^0 values indicate a band structure very similar to Switendick's.

III. ELECTRON ENERGY SHIFTS UNDER STRAIN

A. General considerations

Three different strains are considered here: hydrostatic compression (preserves cubic symmetry), volume-preserving tetragonal, and volume-preserving trigonal. In group-theory language these three strains have Γ_1, Γ_{12}, and $\Gamma_{25'}$ symmetry, respectively (Bouckaert-Smoluchowski-Wigner notation[33]). For cubic crystals an arbitrary strain may be represented (to first order) by a linear combination of these three types of strain.[34]

One must first determine the change in potential due to change in lattice parameters. For the shear strains no change in potential occurs to first order since: (i) We deal with a cubic crystal and our strains are chosen to preserve volume; (ii) we choose a model in which both $V(r)$ and $\Delta V(r)$ are spherically symmetric.[35] The more general statement (valid for noncubic crystals also) for condition (i) is that the strain contain no Γ_1 component.[36] For hydrostatic strain one *does* need $\Delta V(r)$. While this could be done analytically for hydrogen we have chosen to define

$$\Delta V(r) \equiv V^1(r) - V^0(r)\,, \qquad (2)$$

where $V^1(r)$ is computed using the same superposition procedure as used for $V^0(r)$ but with the strained lattice constant

$$a_1 = a_0(1+e)\,, \qquad (3)$$

with $e = -0.01$, i.e., a compression of 1%. For $\Delta\overline{V}$ we calculate both $\overline{V}^0$ and $\overline{V}^1$ using Eq. (1) with the appropriate $V(r)$ and define

$$\Delta\overline{V} \equiv \overline{V}^1 - \overline{V}^0\,. \qquad (4)$$

In applying Eq. (1) here, $r_{\mathrm{mt}} = 1.454\,03$ a.u. for both cases; $r_{\mathrm{WS}} = 1.6400$ a.u. for $\overline{V}^0$ and 1.6236 a.u. for $\overline{V}^1$. Our $\Delta\overline{V} = -0.028\,22$ Ry.

Test of the ΔE program: The perturbation procedure avoids any problems of small differences between large numbers. For a 1% change in lattice constant, however, it is meaningful to simply calculate energy levels (E^1) for the new lattice constant [and $V^1(r)$, $\overline{V}^1$] and take $E^1 - E^0$ as the energy shift. For the hydrostatic case Table II shows the results of this test for Γ_1, X_1, and Σ_1 (at k_F) for $M^2 \simeq 14$. This table clearly indicates that our rather involved computer coding for ΔE by perturbation is correct.

Determination of k_F: It is necessary to determine the k_F values in various directions in $\vec{k}$ space. For this paper we limit the calculation to the three "main" symmetry directions $\langle 001\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$. The procedure for determing k_F is outlined in the Appendix. Table III gives E^0 and ΔE values for the lowest band for k values "at" and near k_F for hydrostatic compression of 1%. For the k values of Table III, as one goes from $k < k_F$ to $k > k_F$, E^0 changes by some 0.05 Ry; the percentage change in ΔE is quite large but the change in

TABLE II. ΔE calculated by our perturbation procedure vs. $E^1 - E^0$ for 1% hydrostatic compression. $a_0 = 4.196\,56$ a.u., $r^0_{\mathrm{mt}} = r^1_{\mathrm{mt}} = 1.454\,03$ a.u., $r^0_{\mathrm{WS}} = 1.64$ a.u., $\overline{V}^0 = -1.396\,67$ Ry; $a_1 = 4.154\,59$ a.u., $r^1_{\mathrm{WS}} = 1.623\,60$ a.u., $\overline{V}^1 = -1.424\,89$ Ry. All energies are in Ry. The units for $\vec{k}$ are $2\pi/a_0$.

State [a]	$\vec{k}$	E^0	$E^1 - E^0$	ΔE
Γ_1	(0,0,0)	3.7192	0.095 11	0.093 09
		−1.9028	−0.032 30	−0.032 28
X_1	(0,0,1)	2.3202	0.053 49	0.052 20
		−0.0316	0.012 29	0.011 71
Σ_1	$(k_F, k_F, 0)$ [b]	1.0504	0.028 35	0.027 47
		−0.5823	−0.003 20	−0.003 57

[a] Reference 33.

[b] For Σ, $k_F = 0.559$.

TABLE III. Shifts in energy for the lowest band at and near k_F for hydrostatic compression ($e = \Delta a/a_0 = -0.01$). $a_0 = 4.196\,56$ a.u., $r^0_{\mathrm{mt}} = 1.454\,03$ a.u., $r^0_{\mathrm{WS}} = 1.64$ a.u., $\overline{V}^0 = -1.396\,67$ Ry. Values of k_x associated with the k_F used in this paper are indicated by an asterisk. All energies are in Ry and are for $M^2 \simeq 14$.

State [a]	Direction	k_x	E^0	ΔE
Δ_1	⟨100⟩	0.778	−0.6085	−0.004 55
		0.786*	−0.5832	−0.003 97
		0.794	−0.5577	−0.003 37
Σ_1	⟨110⟩	0.553	−0.6084	−0.004 20
		0.559*	−0.5823	−0.003 57
		0.565	−0.5561	−0.002 93
Λ_1	⟨111⟩	0.4610	−0.6104	−0.003 09
		0.4685*	−0.5838	−0.002 25
		0.4760	−0.5610	−0.001 50

[a] Reference 33.

magnitude of ΔE is only about a mRy; thus, as far as approximate size of ΔE is concerned, exact location of k_F is not crucial.

B. Hydrostatic (Γ_1) compression

The hydrostatic pressure computation was made with $e = \Delta a/a_0 = -0.01$. The hydrostatic perturbation can be separated into two parts: a "potential part" and a "geometric part." Roughly speaking, the potential part is a $\langle \Psi_0 | \Delta V(r) | \Psi_0 \rangle$-type term where the Ψ_0 are the unperturbed wave functions; more precisely, the potential part is composed of those terms in Appendix C of Ref. 24 which contain either $\Delta V(r)$ or $\Delta \overline{V}$. The geometric part is the *direct* result of a_0 changing to $a_0(1+e)$ and is composed of all the other terms of Appendix C of Ref. 24 which make up ΔE. Since compression makes $V(r)$ more negative, the potential part will always be a negative (downward) shift; the geometric part can be of either sign but will usually by positive. The sign of ΔE for any given E^0 thus depends on the relative sizes of these two parts. Results are given in Table IV for selected $\vec{k}$ points for the two lowest energy bands and for a few higher levels. (Note that K_3 actually lies below the upper K_1 level.)

For compression, for all cases considered the potential part of the energy shift is negative as expected; the geometric part is positive except for the lowest Γ_1 state. The variation in the geometric part is considerably greater than that for the potential part. The general trend is that levels below E_F (approximately) shift downward and levels $\gtrsim E_F$ move upward; shifts at and near E_F are downward and are small relative to the lower-band shifts at Γ, W, X, and K. Γ_1 (bottom of lower band) shifts downward considerably while W_1, X_1, and K_1 (all are above E_F) shift upward. L_1 lies just above E_F and has a very small downward shift. For 1% compression there is a widening of the gap between first and second bands by about 0.005 Ry at W and K and by about 0.002 Ry at X and L. For $k < k_F$ for the Δ and Σ directions there would appear to be considerable widening of the first band-second band gap, the widening at Γ being 0.125 Ry and that at Δ (at k_F) and Σ (at k_F) being about 0.037 and 0.031 Ry, respectively. The widening at Λ (at k_F) is only about 0.007 Ry.

C. Tetragonal (Γ_{12}) strain

This strain is described by $a_z = a_0(1+e)$, $a_x = a_y = a_0(1 - \frac{1}{2}e)$ with $e = 0.01$. Thus volume is preserved and $\Delta e_F = 0$ to first order.[25] As discussed in Sec. III A, $\Delta V(r)$ is taken as zero. The fcc unit cell with lattice constant a_0 is now a body-centered tetragonal (bct) lattice (D^{17}_{4h} space group) with $s = a_0(1+e)$, $t = (\frac{1}{2}a_0)\sqrt{2}(1 - \frac{1}{2}e)$, with the s axis in the orginial z direction, t axes rotated 45° from the original x, y axes. Table V gives tetragonal shifts for selected $\vec{k}$ points for the two lowest energy bands.

From symmetry, shifts for Δ_1, X_1, $X_{4'}$ in the x or y direction are $-\frac{1}{2}\Delta E$ of Δ_1, X_1, $X_{4'}$ in the z direction; X_1 at $(1,0,0)$ was actually calculated and satisfies this symmetry requirement. Shifts for Σ_1, K_1 in the x-z or y-z planes are $-\frac{1}{2}\Delta E$ of the Σ_1, K_1 listed. Shifts for Γ_1, Λ_1, L_1, and $L_{2'}$ are zero by symmetry; Γ_1 and Λ_1 were actually calculated and satisfy this requirement. For the W point, shifts for W_1 at points like $(0, \frac{1}{2}, 1)$ are $-\frac{1}{2}\Delta E$ of W_1 at $(1, 0, \frac{1}{2})$. W_3 is a two-dimensional representation. Under the specific tetragonal strain used here, W_3 at $(1, 0, \frac{1}{2})$ will remain degenerate, while W_3 at points like $(0, \frac{1}{2}, 1)$ will split, the *net* split being $-\Delta E$ of W_3 at $(1, 0, \frac{1}{2})$; the calculated shifts satisfy this requirement.

TABLE IV. Shifts in energy for k_F and for some high-symmetry states for hydrostatic strain ($e = \Delta a/a_0 = -0.01$). a_0, etc., as per Table III. All energies are in Ry and are for $M^2 \simeq 14$. The units for $\vec{k}$ are $2\pi/a_0$. See text for explanation of potential and geometric parts.

State[a]	$\vec{k}$[b]	E^0	ΔE	Potential part of ΔE	Geometric part of ΔE
W_1	$(1, 0, \frac{1}{2})$	0.1604	0.018 57	−0.014 37	0.032 94
X_1	$(0, 0, 1)$	−0.0316	0.011 71	−0.016 11	0.027 81
Δ_1	$(0, 0, k_F)$	−0.5832	−0.003 97	−0.018 46	0.014 50
Γ_1	$(0, 0, 0)$	−1.9028	−0.032 28	−0.019 56	−0.012 72
Λ_1	$(k_F, k_F, k_F$	−0.5838	−0.002 25	−0.017 39	0.015 13
L_1	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	−0.5314	−0.000 11	−0.016 86	0.016 75
K_1	$(\frac{3}{4}, \frac{3}{4}, 0)$	0.0526	0.014 74	−0.015 10	0.029 84
Σ_1	$(k_F, k_F, 0)$	−0.5823	−0.003 57	−0.018 22	0.014 65
W_3	$(1, 0, \frac{1}{2})$	1.1682	0.024 71	−0.021 65	0.046 36
X_4'	$(0, 0, 1)$	0.6090	0.013 49	−0.021 69	0.035 18
Δ_1	$(0, 0, k_F)$	1.3048	0.033 35	−0.018 62	0.051 97
Γ_1	$(0, 0, 0)$	3.7192	0.093 09	−0.016 87	0.109 96
Λ_1	(k_F, k_F, k_F)	0.1596	0.004 98	−0.022 04	0.027 01
L_2'	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	0.0888	0.002 71	−0.022 55	0.025 26
K_1	$(\frac{3}{4}, \frac{3}{4}, 0)$	0.9413	0.019 67	−0.022 78	0.042 45
Σ_1	$(k_F, k_F, 0)$	1.0504	0.027 47	−0.019 72	0.047 18
W_2'	$(1, 0, \frac{1}{2})$	1.2485	0.025 56	−0.023 38	0.048 94
Γ_{15}	$(0, 0, 0)$	4.8330	0.101 67	−0.018 17	0.119 84
K_3	$(\frac{3}{4}, \frac{3}{4}, 0)$	0.8888	c		
Σ_3	$(k_F, k_F, 0)$	1.4794	c		

[a] Reference 33.

[b] For Δ, $k_F = 0.786$; for Λ, $k_F = 0.4685$; for Σ, $k_F = 0.559$.

[c] ΔE was not calculated for these states.

The tetragonal Δ_1 and Σ_1 shifts at E_F are considerably larger than in the hydrostatic case (for the same e). There does not appear to be any overall trend to the tetragonal shifts. Symmetry requires that the "center of gravity" of each band remain fixed.

D. Trigonal ($\Gamma_{25'}$) strain

This strain is described by $\vec{a}_x = a_0[\hat{\imath} + e(\hat{\jmath} + \hat{k})]$, etc., with $e = 0.005$ (stretching along the $\langle 111 \rangle$ axis). Volume is preserved and $\Delta E_F = 0$ to first order.[25] As discussed in Sec. III A, $\Delta V(r)$ is taken as zero. The new symmetry is D_{3d}^5. Table VI gives trigonal shifts for selected $\vec{k}$ points for the two lowest energy bands and a few higher levels.

From symmetry, shifts for Σ and K representations for $\vec{k}$ points described by $(b, 0, b)$, $(0, b, b)$, $(\bar{b}, \bar{b}, 0)$, $(\bar{b}, 0, \bar{b})$, and $(0, \bar{b}, \bar{b})$ will be identical to the appropriate $(b, b, 0)$ shift; ΔE for the other six Σ, K directions will be $-\Delta E$ of the first set. ΔE for Λ_1 in the $(\bar{b}, \bar{b}, \bar{b})$ direction equals the ΔE given; ΔE for the other six Λ directions will be $-\frac{1}{3}$ of the ΔE listed. ΔE for one-dimensional L representations for the other three L directions will be $-\frac{1}{3}$ of the ΔE listed; the calculated L_1 shift at $(\frac{1}{2}, \overline{\frac{1}{2}}, \frac{1}{2})$ satisfies this relation. W_1, X_1, $X_{4'}$, Δ_1, and Γ_1 shifts are zero by symmetry; all but Δ_1 were checked by actual calculation. W_3 is a two-dimensional representation; the B_2 (Y_2') trigonal representation would then show a ΔE of 0.001 79 Ry (not calculated) and the total split would be 0.003 58 Ry.

The trigonal Λ_1 and Σ_1 shifts at E_F are considerably larger than in the hydrostatic case (for $e_{\text{trigonal}} = \frac{1}{2} e_{\text{hydrostatic}}$). As in the tetragonal case, symmetry requires that the "center of gravity" of each band remain fixed. All shifts calculated are downward for one-dimensional representations at $\vec{k}$ points "corresponding" to stretched directions in real space (when a shift is allowed by symmetry).

IV. SUMMARY AND CONCLUSIONS

The general validity of our MPW procedure has been established for the unperturbed fcc hydrogen situation through reasonable agreement with

TABLE V. Γ_{12} strain. Shifts in energy for k_F and for some high-symmetry states for a volume-preserving tetragonal strain: $a_z = a_0(1+e)$, $a_x = a_y = a_0(1-\frac{1}{2}e)$ with $e = 0.01$. a_0, etc., as per Table III. All energies are in Ry and are for $M^2 \simeq 14$. Deformation potentials in units of Ry per unit strain are $100(\Delta E)$. The units for $\vec{k}$ are $2\pi/a_0$.

Unstrained state[a]	Strained state		$\vec{k}$[d]	E^0	ΔE
	b	c			
W_1		P_1	$(1,0,\frac{1}{2})$	0.1604	0.010 37
X_1	Z_1	M_1	$(0,0,1)$	−0.0316	−0.037 88
X_1	X_1	X_1	$(1,0,0)$	−0.0316	0.018 94
Δ_1	Λ_1	Λ_1	$(0,0,k_F)$	−0.5832	−0.026 15
Γ_1	Γ_1	Γ_1	$(0,0,0)$	−1.9028	0.0
Λ_1			(k_F,k_F,k_F)	−0.5838	0.0
K_1	Σ_1	Σ_1	$(\frac{3}{4},\frac{3}{4},0)$	0.0526	−0.016 42
Σ_1	Σ_1	Σ_1	$(k_F,k_F,0)$	−0.5823	0.011 33
W_3		P_3	$(1,0,\frac{1}{2})$	1.1682	0.009 72
W_3	S_3	Y_3	$(0,\frac{1}{2},1)$	1.1682	−0.036 27
W_3	S_4	Y_4	$(0,\frac{1}{2},1)$	1.1682	0.026 55
X_4'	Z_4'	M_4'	$(0,0,1)$	0.6090	−0.041 89
Δ_1	Λ_1	Λ_1	$(0,0,k_F)$	1.3048	−0.046 58
K_1	Σ_1	Σ_1	$(\frac{3}{4},\frac{3}{4},0)$	0.9413	0.001 49
Σ_1	Σ_1	Σ_1	$(k_F,k_F,0)$	1.0504	−0.031 51

[a] Reference 33.

[b] Reference 37; Fig. 9(b). Λ (fcc) reduces to C_s symmetry; see Table III of this reference.

[c] Reference 38; Fig. E2(b).

[d] For Δ, $k_F = 0.786$; for Λ (fcc), $k_F = 0.4685$; for Σ, $k_F = 0.559$.

TABLE VI. Γ_{25}' strain. Shifts in energy for k_F and for some high-symmetry states for a volume-preserving trigonal strain: $\vec{a}_x = a_0[\hat{i} + e(\hat{j} + \hat{k})]$, etc., with $e = 0.005$. a_0, etc., as per Table III. All energies are in Ry and are for $M^2 \simeq 14$. Deformation potentials in units of Ry per unit strain are $200(\Delta E)$. The units for $\vec{k}$ are $2\pi/a_0$.

Unstrained state[a]	Strained state		$\vec{k}$[d]	E^0	ΔE
	b	c			
W_1	B_1	Y_1'	$(1,0,\frac{1}{2})$	0.1604	0.0
X_1	D_1	X_1	$(0,0,1)$	−0.0316	0.0
Γ_1	Γ_1	Γ_1	$(0,0,0)$	−1.9028	0.0
Λ_1	Λ_1	Λ_1	(k_F,k_F,k_F)	−0.5838	−0.030 51
L_1	Z_1	T_1	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	−0.5314	−0.032 76
L_1	A_1	L_1	$(\frac{1}{2},\frac{\bar{1}}{2},\frac{1}{2})$	−0.5314	0.010 92
K_1	Δ_1	Σ_1	$(\frac{3}{4},\frac{3}{4},0)$	0.0526	−0.008 87
Σ_1	Δ_1	Σ_1	$(k_F,k_F,0)$	−0.5823	−0.013 21
W_3	B_1	Y_1'	$(1,0,\frac{1}{2})$	1.1682	−0.001 79
X_4'	D_4	X_4	$(0,0,1)$	0.6090	0.0
Λ_1	Λ_1	Λ_1	(k_F,k_F,k_F)	0.1596	−0.033 37
L_2'	Z_2'	T_2'	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	0.0888	−0.030 84
K_1	Δ_1	Σ_1	$(\frac{3}{4},\frac{3}{4},0)$	0.9413	−0.016 35
Σ_1	Δ_1	Σ_1	$(k_F,k_F,0)$	1.0504	−0.006 72
K_3	Δ_1	Σ_1	$(\frac{3}{4},\frac{3}{4},0)$	0.8888	−0.002 80
Σ_3	Δ_1	Σ_1	$(k_F,k_F,0)$	1.4794	−0.008 70

[a] Reference 33.

[b] Reference 37; Fig. 16(b).

[c] Reference 38; Fig. E4(b).

[d] For Λ, $k_F = 0.4685$; for Σ, $k_F = 0.559$.

Switendick's APW calculations[16] when his parameters are used. (The general validity of the MPW method has long been established.[20-23]) The perturbation procedure has been tested by comparison of ΔE and E^1-E^0 and by earlier work.[24,25]

For fcc hydrogen under hydrostatic compression (see Tables III and IV) the general trend is that levels $\lesssim E_F$ shift downward and levels $\gtrsim E_F$ move upward; shifts at and near E_F are downward and are relatively small. There is a general widening of the gap between first and second bands, and the "center of gravity" of the second band shifts upward considerably; that of the first band appears to be relatively stationary.

A much more extensive calculation would be needed to determine ΔE_F and the change in the overall density of states at E_F. The Δ_1 and Σ_1 shifts near E_F are such as to give E vs $\vec{k}$ a steeper slope (see Table III) contributing to a decreased density of states if ΔE_F is small. For Λ_1 near E_F there is also a steepening of slope but the contribution to change in density of state is difficult to assess as we are near a region of high curvature of E vs $\vec{k}$.

For the shear strains (see Tables V and VI) the numerical results agree with symmetry predictions where tested. For comparable e, the shear shifts at E_F (when allowed by symmetry) are considerably larger than the corresponding hydrostatic shifts.

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APPENDIX: DETERMINATION OF k_F

We first attempted to simply take k_F values from Switendick's[16] Fig. 1; this led, however, to E^0 values which differed considerably among the three directions chosen. The E vs $\vec{k}$ lines in question have quite steep slopes in this region.) We then used the following procedures: For a trial expansion function containing a large number of symmetrized plane waves ($M^2 \simeq 40$) our MPW energy levels are about 0.02 Ry above Switendick's APW values. As his E_F is -0.607 Ry we choose -0.590 Ry as "our" E_F; we then calculated E^0 for two k values near k_F in each of the three directions considered and determined a "final k_F" graphically. In the actual perturbation calculations far fewer plane waves are used than in the determination of k_F. Various tests indicate that the difference in ΔE between small M^2 (14) and large M^2 (40) is quite small (on the order of 0.0005 Ry) compared to the difference in E^0 (on the order of 0.01 Ry); i.e., ΔE "converges" faster than E^0. Thus E_F in our actual perturbation calculations is about -0.583 Ry and will differ slightly between the various directions in $\vec{k}$ space.

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[29] Our superposition procedure may be readily checked: our value for charge inside r_{mt} is 0.8193, Switendick gives 0.82; our preliminary calculation value for $V(r_{\mathrm{mt}})$ is −1.4077 Ry, Switendick gives −1.407 Ry (his $\overline{V}$ value of −1.354 Ry minus the 0.53-Ry discontinuity at r_{mt}).

[30] For fcc hydrogen, using the same a_0, r_{mt}, and $\overline{V}$, the change from the $-2/r$ crystal potential (simply cut off at r_{mt}) to a superposition potential raises the energy levels at high-symmetry $\vec{k}$ points by about 0.1 Ry.

[31] While the reduction chosen allows for 2% compression, the actual compression used in the calculation reported here is only 1%.

[32] Using a_0, r_{mt}, and $\overline{V}$ as in the calculation for Table I and changing only $\overline{V}$ from −1.354 Ry (Switendick's value) to −1.394 10 Ry (our average for this r_{mt}) lowered the energy levels tested by about 0.01 Ry. Reducing r_{mt} by 2% and making the corresponding change in $\overline{V}$ (to −1.396 67 Ry) caused further changes in E^0 by about 0.001 Ry.

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