Erratum: Thermal and magnetic properties of landau quantized group VI dichalcogenide carriers in the approach to the degenerate limit (2020 J. Phys. Commun. 4 095006)

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Due to an error in the production process an earlier version of this article was inadvertently published. Below are the few typographical corrections that were missed.

LIST OF CORRECTIONS

1. In the list of key words, ‘magnetic field’ should be replaced by ‘de Haas-van Alphen oscillations’.
2. In section 2, second line, ‘moment’ should be ‘moments’.
3. In section 2, third line, ‘Hamiltonian is’ should be ‘Hamiltonians are’.
4. In section 2, fourth line, after ‘Green’s function’, the semi-colon should be a colon.
5. In section 3, line above equation (3.1), the term ‘equation (1.9)’ should be followed by an insertion of the word ‘is’.
6. In equation (3.6), there are (properly) two ‘\(=\)’ signs. Just before the second one, on the right, there should be three dots ‘…’ on main line, similar to those of the corresponding terms on the left. The correct equation should be:

\[
\oint dz = \oint dz_1 \cdots + \oint dz_n = (1 + e^{-\pi i (E_j - \pi - x)}) \int dz e^{z} e^{\pi i (E_j - \pi - x)} \sin(z) = 1.
\]

7. In equation (3.11) on the second line of the equation, after the multiplication sign, the opening curly bracket is too small—it should be bigger to be comparable in size with the closing curly bracket at the end of the third line of the equation.
8. On the second line below equation (3.14), in about the middle of the line, there is a comma before ‘(3.13)’. The word ‘Eqns.’ should be between the comma and before the ‘(3.13)’.
9. In section 5, on line 10, change the square brackets to magnitude signs in ‘\([\mu - E_j]\); The same should be done on line 15.
10. In reference 20, the page numbers should read ‘213–215’.
11. In references [29] and [30], journal name should be ’Phys. Rev. B’ rather than ’Phys. Rev.’.

The publisher sincerely apologises for any inconvenience caused by this error and can confirm that the final results of the paper remain unaffected.

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1. Introduction

This paper addresses some fundamental physical properties of 'Dirac–like' materials, in particular the Group VI Dichalcogenides. Starting with Graphene [1–6], such materials have been at the focus of research attention since the discovery of the extraordinary electrical conduction and detection properties of Graphene about fifteen years ago. Additional materials of this type include Silicene [7], Topological Insulators [8], as well as the Dichalcogenides [9] (and some others). All are under intense investigation worldwide in all science and engineering disciplines for their potential to succeed Silicon as the material of choice for the next generation of electronic devices and computers. Recognition of the importance of these materials has been underscored by the award of the 2010 Nobel Prize in Physics to Geim and Novoselov for their pioneering work on Graphene. The fact that the low energy carrier spectrum of 'Dirac–like' materials mimics that of relativistic electrons/positrons (with energy linearly proportional to momentum) also heightens intellectual interest in them as accessible solid state laboratories of relativistic physics, albeit with different parameters. Much has already been done in regard to experimental and theoretical studies on Graphene, and considerable work on the other 'Dirac–like' materials is now filling the scientific and engineering literature. Here, we address the magnetic response and the thermodynamic properties of Group VI Dichalcogenides [9] to study their behavior subject to Landau quantization in a high magnetic field, particularly in the degenerate regime and also above the zero–temperature limit. It should be remarked that all the results obtained here are directly applicable to other pseudospin–1/2 Dirac materials, Graphene in particular, by setting the energy shift \( E_g \to 0 \) and \( g \to 0 \) (section 2), and appropriately adjusting the numerical value of the characteristic speed \( \gamma \) of the underlying linear low energy band structure approximation.

In regard to the thermal properties of matter and the calculation of their temperature dependence, the entropy is of central importance: determination of the entropy is essential for evaluation of the specific heat, which we present as an example for the Landau–quantized Dichalcogenides. As the associated Dichalcogenide spectrum has an unusual unbounded negative energy component, we verify that the usual positivity of entropy and its vanishing at zero temperature still apply, and stand as guiding requirements on the validity of approximate procedures for calculations of temperature dependence of the statistical thermodynamic properties of Group VI Dichalcogenides.
functions. Here, we examine these functions in the degenerate statistical regime, including determination of their temperature dependence in the approach to zero temperature. In view of the great importance of the magnetic field as an agent for probing the properties of matter and also modifying them [10, 11], particularly with Landau quantization of orbits, we address its role in the statistical thermodynamics of the Group VI Dichalcogenides jointly with that of temperature, as reflected in the entropy and specific heat of these systems. Furthermore, the results are applied to the analysis of the magnetic moments of the Group VI Dichalcogenides and their de Haas–van Alphen (dHaVA) oscillatory phenomenology due to Landau quantization.

The basic formulation of our study of statistical thermodynamics employs Green’s functions, as set forth below in this section. The pertinent Dichalcogenide Green’s functions are reviewed in detail in section 2. Section 3 presents our calculations of the temperature and magnetic field dependencies of the Grand Potential, Helmholtz Free Energy and magnetic moment in the degenerate regime, including the approach to the zero temperature limit. Entropy and the specific heat of the Landau quantized Dichalcogenides are analyzed in the degenerate regime in section 4, again including temperature dependence in the approach to zero temperature. Some qualitative features of our results are discussed in section 5, including de Haas–van Alphen oscillatory phenomenology of the Group VI Dichalcogenides.

Our use of a retarded Green’s function $G^{ret}$ in the determination of statistical thermodynamic functions is based on the fact that its trace in position–time representation produces the ordinary (‘classical’) partition function $\tilde{Z}(\beta) = \text{Tr} \exp(-\beta H)$ with the substitution $T \rightarrow -i\beta$ as [12]

$$\tilde{Z}(\beta) = \int d\vec{x} \text{Tr}(iG^{ret}_{T\geq 0}(\vec{x}, \vec{x}'; T \rightarrow -i\beta)),$$

(1.1)

where $\beta = 1/k_B T'$ is inverse thermal energy, $k_B$ is the Boltzmann constant, $T'$ is Kelvin temperature, and $\text{Tr}$ denotes the trace. This is readily verified using the definition of the Green’s function in terms of a time translation operator [12]. Actually, it is the logarithm of the grand partition function $Z(\beta)$ for Fermions that is required to determine the Grand Potential, $\Omega$, and the Helmholtz Free Energy, $F$, and Wilson’s book [13] reports a clever way to obtain it from the ordinary partition function $\tilde{Z}(\beta)$, as follows ($\mu$ is chemical potential, $N$ is particle number and $E_\gamma$ represents the single–fermion energy spectrum):

$$\Omega = F - \mu N = -k_B T' \ln Z = -k_B T' \sum_{E_\gamma} \ln(1 + e^{-\beta(E_\gamma - \mu)}),$$

(1.2)

and writing the $E_\gamma$-summand $(B(E))$ as an inverse Laplace transform ($\int ds$ represents integration over the inverse Laplace transform contour in the complex $s$-plane)

$$B(E) \equiv -k_B T' \ln(1 + e^{-\beta(E - \mu)}) = \int_{c-i\infty}^{c+i\infty} ds \frac{e^{E s}}{2\pi i} p(s)$$

(1.3)

with $p(s)$ as the Laplace transform of $B(E)$

$$p(s) = \int_{c-i\infty}^{c+i\infty} dE \ e^{-iE B(E)},$$

(1.4)

we have

$$\Omega = F - \mu N = \int_{c-i\infty}^{c+i\infty} ds \frac{dE}{2\pi i} p(s) \sum_{E_\gamma} e^{E_\gamma} = \int_{c-i\infty}^{c+i\infty} ds \frac{dE}{2\pi i} p(s) \tilde{Z}(\beta \rightarrow -s).$$

(1.5)

This expresses $\Omega$ and $F$ in terms of the ordinary partition function ($\tilde{Z}$), or alternatively, the Green’s function. Noting that rewriting equation (1.5) in the form [13]

$$\Omega = F - \mu N = \int_{c} ds \frac{dE}{2\pi i} \left( \tilde{Z}(\beta \rightarrow -s) \frac{s^2 p(s)}{2\pi} \right),$$

(1.6)

one may employ a useful special case of the convolution theorem for Laplace transforms [14] to obtain

$$\Omega = F - \mu N = \int_{0}^{\infty} dE \int_{c} ds \frac{dE'}{2\pi i} e^{E' s} \tilde{Z}(s) \frac{(s')^2 p(s')}{2\pi i} \int_{c} ds' \frac{dE'}{2\pi i} e^{E' s'} p(s'),$$

(1.7)

and since

$$\int_{c} \frac{ds'}{2\pi i} e^{E' s'} p(s') = \frac{\partial^2}{\partial E^2} \int_{c} \frac{ds'}{2\pi i} e^{E' s'} p(s') = \frac{\partial^2 B(E)}{\partial E^2} = \frac{\partial f_0(E)}{\partial E},$$

(1.8)

we have the convenience of dealing directly with the temperature dependent Fermi distribution $f_0(E)$ (rather than $B(E)$):
\[ \Omega = F - \mu N = \int \frac{ds}{2\pi i} \frac{\tilde{Z}(s)}{s^2} \int_0^\infty dE \ e^{iE} \frac{\partial f_n(E)}{\partial E} = -\frac{\beta}{4} \int \frac{ds}{2\pi i} \frac{\tilde{Z}(s)}{s^2} \int_0^\infty dE \ e^{iE} \text{sech}^2 \left( \frac{E - \mu \mid \beta}{2} \right). \]  

(1.9)

2. Retarded Green’s function of group VI dichalcogenides in a magnetic field

As indicated above, our approach to the determination of the role of a quantizing magnetic field in the magnetic moment and statistical thermodynamic functions of charge carriers of the Group VI Dichalcogenides in the low energy regime (in which their Hamiltonian is ‘Dirac–like’ with energy proportional to momentum) is undertaken using the retarded Green’s function; in earlier work [15], the associated Landau–quantized Green’s function matrix was derived with full account of its pseudospin–1/2 and spin–1/2 features in the presence of a high magnetic field; and the pertinent diagonal elements of its retarded Green’s function pseudospin matrix \( G^\text{ret}_{11} \) are given in 2D–position (\( \vec{R} = \vec{x} - \vec{x}' \)), time (\( T = t - t' \)) representation as \( \hbar \to 1 \)

\[ iG^\text{ret}_{11}(\vec{x}, \vec{x}'; T) = \eta_n(T) \exp \left( \frac{i\epsilon}{2} [\vec{x} \cdot \vec{B} \times \vec{x}'] \right) \frac{eB}{4\pi} e^{-i\epsilon_n T} \exp \left( -\frac{eBR^2}{4} \right) \times \sum_{n=0}^{\infty} L_n \left( \frac{eBR^2}{2} \right) \left\{ \cos \left( \sqrt{g^2 + \epsilon^2_{n\pm}} T \right) \mp \frac{ig}{\sqrt{g^2 + \epsilon^2_{n\pm}}} \sin \left( \sqrt{g^2 + \epsilon^2_{n\pm}} T \right) \right\}. \]  

(2.1)

\( (G^\text{ret}_{11} \) represents \( G^\text{ret}_{11} \) or \( G^\text{ret}_{22} \) corresponding to the upper or lower of alternative signs on the right of equation (2.1)). Here, \( \eta_n(T) = 1 \) for \( T > 0 \); \( 0 \) for \( T < 0 \) is the Heaviside unit step function. A spin index \( s_z = \pm 1 \) enters into energy shifts as \( E_n = \pm \nu \lambda \) with \( \nu = \pm 1 \) as the valley index; furthermore, \( \lambda \) is the spin splitting and \( g = \pm \frac{\Delta}{2} - E_n \) with \( \Delta \) as the energy gap without spin splitting. Also, \( L_n \) represents the Laguerre polynomials and \( \epsilon^2_{n\pm} \) is given by \( (L_n \equiv \text{sign} (\nu) \equiv \pm 1) \)

\[ \epsilon^2_{n\pm} = (2n + 1 \mp 1) \gamma \gamma eB, \]  

(2.2)

and \( \gamma \) is an effective speed determined by the tight binding hopping parameter and lattice spacing. It is useful to rewrite the trace of equation (2.1) in the following form (for use below):

\[ \text{Tr}(iG^\text{ret}_{11}(\vec{x}, \vec{x}'; T)) = \exp \left( \frac{i\epsilon}{2} [\vec{x} \cdot \vec{B} \times \vec{x}'] \right) \frac{eB}{4\pi} e^{-i\epsilon_n T} \exp \left( -\frac{eBR^2}{4} \right) \times \sum_{s_z=\pm 1} \sum_{\nu=\pm 1} \sum_{n=0}^{\infty} \sum_{n'=-n}^{n} L_n \left( \frac{eBR^2}{2} \right) \left( 1 \mp (\nu') \frac{g}{\sqrt{g^2 + \epsilon^2_{n\pm}}} \right) e^{\pm \epsilon n' T}. \]  

(2.3)

This trace encompasses sums over the spin index \( s_z = \pm 1 \), valley index \( \nu = \pm 1 \), pseudospin index \( \pm \), the signature \( \pm' \) of exponentials constituting sine and cosine functions and the Laguerre sum index \( n \to \infty \). For the problem at hand, \( \vec{x} \equiv \vec{x}' \), \( \vec{R} \equiv 0 \) and \( L_n(0) \equiv 1 \), whence

\[ \int d\vec{x} \text{ Tr}(iG^\text{ret}_{11}(\vec{x}, \vec{x}'; T)) = (\text{area}) \frac{eB}{4\pi} e^{-i\epsilon_n T} \times \sum_{s_z=\pm 1} \sum_{\nu=\pm 1} \sum_{n=0}^{\infty} \sum_{n'=-n}^{n} \left( 1 \mp (\nu') \frac{g}{\sqrt{g^2 + \epsilon^2_{n\pm}}} \right) e^{\pm \epsilon n' T}, \]  

(2.4)

where the (area) factor arises from the 2D \( d\vec{x} \)–integration; this area factor will henceforth be taken as unity, and \( \Omega, \Gamma, \tilde{Z} \) and entropy \( S \), magnetic susceptibility \( M \) and specific heat \( C_V \) are to be understood on a per–unit–area basis, with \( N \to n \)–density.

It is also of interest to describe the thermodynamic Green’s function matrix \( G(\vec{x}, \vec{x}'; T) \), which is characterized by periodicity in imaginary time (period \( \tau = -i\beta = -i/k_B T \)) instead of retardation. It may be written in terms of its ‘greater’ \( G^> \) and ‘lesser’ \( G^< \) constituents as \([12, 15]\)

\[ G(\vec{x}, \vec{x}'; T) = \eta_n(T) G^>(\vec{x}, \vec{x}'; T) + \eta_n(-T) G^<(\vec{x}, \vec{x}'; T). \]  

(2.5)

The matrix Green’s function constituents \( G^> \) and \( G^< \) define a corresponding spectral weight matrix \( A \) as

\[ G^>(\vec{x}, \vec{x}'; T) - G^<(\vec{x}, \vec{x}'; T) = -iA(\vec{x}, \vec{x}'; T) = -i \int \frac{d\omega}{2\pi} e^{-i\omega T} A(\vec{x}, \vec{x}'; \omega). \]  

(2.6)
Here, \( G^\tau(\vec{x}, \vec{x}'; T), G^\sigma(\vec{x}, \vec{x}'; T) \) and \( A(\vec{x}, \vec{x}'; T) \) all satisfy the homogeneous counterpart of the Green’s function equation; and all involve the same Peierls phase factor \( \exp(^i\frac{\xi}{2} [\vec{x} \cdot \vec{B} \times \vec{x}']) \) which we divide out, defining \( A'(\vec{x}, \vec{x}'; T) \) by the relation
\[
A(\vec{x}, \vec{x}'; T) = \exp \left( ^i\frac{\xi}{2} [\vec{x} \cdot \vec{B} \times \vec{x}'] \right) A'(\vec{x}, \vec{x}'; T).
\] (2.7)

The constituent parts of the thermodynamic Green’s function matrix may be determined from the spectral weight function matrix in frequency representation as
\[
i\gamma(\vec{x}, \vec{x}'; \omega) = \left\{ \begin{array}{ll} -f_0(\omega) & \text{for } A'(\vec{x}, \vec{x}'; \omega), \\ -f_0(\omega) & \text{for } A'(\vec{x}, \vec{x}'; \omega), \\ 1 & \text{for } A'(\vec{x}, \vec{x}'; \omega), \end{array} \right.
\] (2.8)

where \( f_0(\omega) \) is the Fermi–Dirac distribution function. Furthermore \( A'(\vec{x}, \vec{x}'; \omega) \) may be determined from the structure of the retarded Green’s function \( G^{\text{ret}} \) in frequency representation using the relation \( (\vec{R} = \vec{x} - \vec{x}') \)
\[
A'(\vec{x}, \vec{x}'; \omega) = -2\text{Im}G^{\text{ret}}(\vec{R}; \omega),
\] (2.9)

leading to the result for its diagonal elements \( A'_{11}(\vec{x}, \vec{x}'; \omega) \) as [15]
\[
A'_{11}(\vec{x}, \vec{x}'; \omega) = \frac{eB}{2} \exp \left( -\frac{eBR^2}{4} \right) \left( 1 \pm \frac{g}{\omega - E_n} \right) \sum_{n=0}^{\infty} \sum_{\pm} L_n \left( \frac{eBR^2}{2} \right) \times \delta(\omega - E_n \pm ' \sqrt{g^2 + e_n^2}).
\] (2.10)

From this, the diagonal elements of the thermodynamic Green’s function matrix may be determined for the Dichalcogenides in a magnetic field using equation (2.8). In particular, we obtain \( TrG^\tau(\vec{x}, \vec{x}'; T) \) as
\[
-\text{i} TrG^\tau(\vec{x}, \vec{x}'; T) = \exp \left( \frac{i\pi}{2} [\vec{x} \cdot \vec{B} \times \vec{x}'] \right) \frac{eB}{4\pi} \sum_{s_z=\pm 1} \sum_{\pm} \sum_{n=0}^{\infty} \sum_{\pm} \sum_{\pm} \left( 1 \pm \frac{(\pm 1)g}{\sqrt{g^2 + e_n^2}} \right) e^{-iE_n \pm ' \sqrt{g^2 + e_n^2}}.
\] (2.11)

The density \( n \) follows as
\[
n = -\text{i} TrG'_{11}(\vec{R} = 0; T = 0) = \frac{eB}{4\pi} \sum_{s_z=\pm 1} \sum_{\pm} \sum_{n=0}^{\infty} \sum_{\pm} \sum_{\pm} \left( 1 \pm \frac{(\pm 1)g}{\sqrt{g^2 + e_n^2}} \right) \times f_0 \left( E_n \pm ' \sqrt{g^2 + e_n^2} \right).
\] (2.12)

3. Temperature dependence of the grand potential and magnetic moment: degenerate regime and also above the zero–temperature limit

The analysis of temperature dependence devolves upon a careful evaluation of the Grand Potential \( \Omega \) and Helmholtz Free Energy \( F \), and we examine this in the approach to the degenerate regime, \( \mu \beta \to \infty \), by rewriting equation (1.9) with a change of variable, \( z = [E - \mu] \beta / 2 \); the resulting \( \text{E-integral} \) of equation (1.9) given by
\[
\int_0^\infty dE_z \cdots \equiv \int_0^\infty dE \ \text{sech}^2 \left( \frac{[E - \mu] \beta}{2} \right) = \frac{2}{\beta} e^\mu \int_{-\beta / 2}^{\infty} dz \ e^{2\mu z / \beta} \text{sech}^2 z,
\] (3.1)

and in the degenerate regime only the even part of the exponential integrand contributes, \( e^{2\mu z / \beta} \to \cosh(2z / \beta) \), with the result [16]
\[
\int_0^\infty dE_z = \frac{4\pi}{\beta^2} \frac{se^{\mu}}{\sin(\frac{\mu}{\beta})}.
\] (3.2)

Therefore, we obtain equation (1.9) as
\[
\Omega = F - \mu N = -\frac{\pi}{\beta} \int_c^{d} \frac{ds}{2\pi i} \frac{e^{\mu s} Z(s)}{s \sin(\pi s / \beta)}.
\] (3.3)

Employing equations (1.5) and (2.4) and noting our successive changes in the argument of \( Z \) (summarized as \( T \to -is \) in the Green’s function trace; also note that \( L_n(0) \equiv 1 \) and set \( s = \beta s' \)), we have
\[
\Omega = F - \mu n = -\frac{eB}{4\pi} \sum_{\nu = \pm 1} \sum_{\nu = \pm 1} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \left( 1 \mp (\pm 1) \frac{g}{\sqrt{g^2 + \epsilon_{n^+}^2}} \right)
\times \int_{0}^{\infty} \frac{ds}{2\pi i} \exp \left[ s^2 \beta (\mu - E_n \pm \sqrt{g^2 + \epsilon_{n^+}^2}) \right] \\
\times \frac{\exp \left[ \frac{g}{\sqrt{g^2 + \epsilon_{n^+}^2}} \right]}{\sin(\pi s^2)}
\] (3.4)
on a per-unit-area basis \((F \to F/\text{area} \text{ and } n = N/\text{area}).

To evaluate the \(s^2\)-integral of equation (3.4), we exponentiate the integrand factor as \(1/s^2 = \beta \int_{0}^{\infty} dx \ e^{-\beta s^2 x}\) so that \((z = \pi s^2)\)

\[
\int_{0}^{\infty} \frac{ds'}{2\pi i} \frac{e^{\beta \mu_s}}{\sin(\pi s')^2} = \beta \int_{0}^{\infty} \frac{dz}{2\pi i} \frac{e^{\beta [E_n - E_n - x]}}{\sin(z)}.
\] (3.5)

Noting that the contour of \(z\)-integration along \(c\) is a straight line from \(z = -i\infty + 0^+ \text{ to } +i\infty + 0^+\), we consider closing the contour \([17]\) with a parallel line \((c')\) from \(i\infty - \pi^+ \text{ to } -i\infty - \pi^+\) on which \(dz' = -dz_c\) and \(\sin(z') = -\sin(z).\) Moreover, the closed contour integrand \(\oint = \int_c + \int_{c'}\) has the residue \(1\) at \(z = 0\), so that

\[
\oint dz = \int_c dz_c \ldots + \int_{c'} dz_c' = (1 + e^{-\beta [E_n - E_n - x]}) \int_c dz \frac{e^{\beta [E_n - E_n - x]}}{\sin(z)} = 1.
\] (3.6)

Consequently, the \(x\)-integration of equation (3.5) is given by

\[
\int_{0}^{\infty} dx \frac{1}{1 + e^{-\beta [E_n - E_n - x]}} = \frac{1}{\pi \beta} \ln(1 + e^{\beta [E_n - E_n - x]}).
\] (3.7)

and, for the degenerate regime under consideration, we obtain the Grand Potential \(\Omega\) as

\[
\Omega = F - \mu n = -\frac{eB}{4\pi} \sum_{\nu = \pm 1} \sum_{\nu = \pm 1} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \left( 1 \mp (\pm 1) \frac{g}{\sqrt{g^2 + \epsilon_{n^+}^2}} \right)
\times \ln(1 + \exp \left[ \beta (\mu - E_n \pm \sqrt{g^2 + \epsilon_{n^+}^2}) \right]).
\] (3.8)

This indicates the behavior at very low temperature to be given approximately by \(\eta_n (x) = 1\) for \(x > 0, 0\) for \(x < 0\) and \(\eta_n (x) = 1\) for \(x < 0, 0\) for \(x > 0; \eta_n (x) = 1\) for all \(x)\)

\[
\Omega = F - \mu n = -\frac{eB}{4\pi} \sum_{\nu = \pm 1} \sum_{\nu = \pm 1} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \left( 1 \mp (\pm 1) \frac{g}{\sqrt{g^2 + \epsilon_{n^+}^2}} \right)
\times \left\{ \eta_n (\mu - E_n \pm \sqrt{g^2 + \epsilon_{n^+}^2}) \left[ \mu - E_n \pm \sqrt{g^2 + \epsilon_{n^+}^2} \right] \\
+ \beta^{-1} \exp \left( -\beta |\mu - E_n \pm \sqrt{g^2 + \epsilon_{n^+}^2} | \right) \right\},
\] (3.9)
on a per-unit-area basis. The last term of equation (3.9) includes exponentially small temperature corrections from energies both above and below the Fermi level \(\mu\).

The results exhibited above in equations (3.8, 9) for the Grand Potential and Helmholtz Free Energy in the degenerate regime clearly exhibit the effects of the quantizing magnetic field jointly with those of finite temperature. To elaborate further on the role of the magnetic field we evaluate the magnetic moment, \(M\), which may be obtained from the free energy as (per unit area)

\[
M = \frac{\partial F}{\partial B} = -\frac{\partial (F - \mu n)}{\partial B} - \frac{\partial n}{\partial B} = \Delta M = -\frac{\partial n}{\partial B}.
\] (3.10)

and we write \(\Delta M = \Delta M_{\text{deg}} (T' = 0) + \Delta M_{\text{deg}} (T' > 0)\) where differentiation of the terms of equation (3.9) with respect to \(B\) yields

\[
\Delta M_{\text{deg}} (T' = 0) = \frac{e}{4\pi} \sum_{\nu = \pm 1} \sum_{\nu = \pm 1} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \sum_{n = 0}^{\infty} \left( \mu - E_n \pm \sqrt{g^2 + \epsilon_{n^+}^2} \right)
\times \left\{ \frac{(\pm 1)g}{\sqrt{g^2 + \epsilon_{n^+}^2}} \pm \frac{(\pm 1)g \epsilon_{n^+}^2}{2(g^2 + \epsilon_{n^+}^2)^{3/2}} \right\}
\times \left\{ 1 \mp (\pm 1) \frac{g \epsilon_{n^+}^2}{2\sqrt{g^2 + \epsilon_{n^+}^2}} \right\},
\] (3.11)
and

$$\Delta M_{\text{deg}}(T' > 0) = \frac{e}{4\pi} \sum_{i=\pm 1} \sum_{s=\pm 1} \sum_{\gamma} \sum_{n=0}^{\infty} \left( 1 \pm (\pm') \frac{g}{\sqrt{g^2 + e_{\pm}^2}} \right) \times e^{-\beta g - E_{i'}(\sqrt{g^2 + e_{\pm}^2} + E_{i'}(\sqrt{g^2 + e_{\pm}^2})}$$

$$\times \left( \beta - 1 \right) \left( \eta_i - \eta_i' \right) \frac{e_{\pm}^2}{2(\sqrt{g^2 + e_{\pm}^2})^2}.$$  \hspace{1cm} (3.12)

where \( \eta_i - \eta_i' \equiv \eta_i (\mu - E_i + \sqrt{g^2 + e_{\pm}^2}) - \eta_i' (\mu - E_i + \sqrt{g^2 + e_{\pm}^2}). \) The last term of \( M(-\mu \partial n/\partial B) \) may be evaluated by differentiating equation (3.12), with the result

$$-\frac{\partial n}{\partial B} = -\frac{\mu e}{4\pi} \sum_{i=\pm 1} \sum_{s=\pm 1} \sum_{\gamma} \sum_{n=0}^{\infty} \left( 1 \pm (\pm') \frac{g}{\sqrt{g^2 + e_{\pm}^2}} \right) \frac{\beta}{2}\text{sech}^2 \left( \frac{E_{i'}(\sqrt{g^2 + e_{\pm}^2}) - \mu}{} \right) \times \left( \frac{\beta}{\sqrt{g^2 + e_{\pm}^2}} \right)$$

$$\pm \frac{(\pm')g\epsilon_{\pm}^2}{2(\sqrt{g^2 + e_{\pm}^2})^2} f_0(E_{i'}(\sqrt{g^2 + e_{\pm}^2})).$$ \hspace{1cm} (3.13)

In regard to the final magnetic moment contribution from \(-\mu \partial n/\partial B\) in the degenerate limit of zero temperature, we have

$$\left(-\frac{\partial n}{\partial B}\right)_{\text{deg}} = -\frac{\mu e}{4\pi} \sum_{i=\pm 1} \sum_{s=\pm 1} \sum_{\gamma} \sum_{n=0}^{\infty} \left( 1 \pm (\pm') \frac{g}{\sqrt{g^2 + e_{\pm}^2}} \right) \times \eta_i (\mu - E_{i'}(\sqrt{g^2 + e_{\pm}^2}) - \delta(\mu - E_{i'}(\sqrt{g^2 + e_{\pm}^2}))$$

$$\pm \frac{(\pm')g\epsilon_{\pm}^2}{2(\sqrt{g^2 + e_{\pm}^2})^2} \eta_i (\mu - E_{i'}(\sqrt{g^2 + e_{\pm}^2})).$$ \hspace{1cm} (3.14)

and finite temperature corrections are exponentially small, proportional to \( \exp(-\beta E_{i'}(\sqrt{g^2 + e_{\pm}^2}) - \mu). \)

Taken jointly with equations (3.11)–(3.12), (3.13)–(3.14) complete the determination of the magnetization, \( M = \Delta M - \mu \partial n/\partial B. \)

4. Entropy and specific heat of the group VI dichalcogenides: temperature dependence in the degenerate regime and also above the zero–temperature limit

The entropy, \( S \), is determined by a variation of the Helmholtz Free Energy, \( F \), in the thermodynamic relation [18]

$$dF = -pdV - SdT + \mu dN$$

\( (p \) is pressure (linear in 2D), \( \mu \) is chemical potential, \( T' \) is Kelvin temperature, \( N \) is number and \( V \) is volume (area in 2D)). Holding \( N \) and \( V \) constant, the entropy (per unit area) may be identified as

$$S = \left( -\frac{\partial F}{\partial T'} \right)_{N,V,\mu} = -\frac{\partial \Omega}{\partial T'} - \frac{n}{\partial \mu} = k_B \beta^2 \frac{\partial \Omega}{\partial \beta}. \hspace{1cm} (4.1)$$

In considering \( \left( \partial F/\partial T' \right)_{N,V,\mu} \), it should be noted that only the explicit dependence of \( F(\beta, \mu) \) on \( \beta \) contributes, to the exclusion of implicit dependence on \( \beta \) through \( \mu \) (as determined by the expression for density \( n(\beta, \mu) \)), since such a contribution would be of the form \( \partial F/\partial \mu \times \partial \mu/\partial \beta \), which vanishes identically because

$$\partial F/\partial \mu \equiv 0,$$

by definition of the density \( n \). In this context the \( \mu \)-dependence of \( F \) cannot contribute to \( \partial F/\partial T' \), so the term \(-n \partial \mu/\partial T' \) in equation (4.1) must be understood to vanish.

As we are dealing with the statistical thermodynamics of an unusual system, which has an unbounded negative component of its energy spectrum (in addition to the more usual unbounded positive component), it is of interest to verify that the usual basic features of the entropy still apply to the system under consideration. The first feature to verify is that the entropy vanishes in the zero temperature limit, \( \beta \to \infty \): this is readily verified from equation (3.3), whose low temperature limit is given by
\[
[\Omega]_{\beta > 1} = [F - \mu n]_{\beta > 1} = -\int ds \frac{e^\mu \tilde{Z}(s)}{s^2} + 0\left(\frac{1}{\beta^2}\right) \text{ for } \beta \gg 1,
\]

whence

\[
S_{T \to 0} = -\frac{\partial}{\partial T} [F - \mu n] - \mu \frac{\partial n}{\partial T} = 0. \quad (4.2)
\]

An alternative, fully general, proof based on equation (1.2) follows:

\[
-\frac{\partial \Omega}{\partial T} - \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \left( \beta^{-1} \sum_{E_i} \ln (1 + e^{-\beta(E_i - \mu)}) \right)
\]

\[
= k_B \beta^2 \sum_{E_i} \left\{ \beta^{-2} \ln (1 + e^{-\beta(E_i - \mu)}) + \beta^{-1} e^{-\beta(E_i - \mu)} [E_i - \mu] \right\}
\]

\[
= k_B \sum_{E_i} \ln (1 + e^{-\beta(E_i - \mu)}) + k_B \beta \sum_{E_i} [E_i - \mu] f_0(E_i - \mu). \quad (4.3)
\]

and in the limit of zero temperature (\(\beta \to \infty\)), the entropy vanishes

\[
S = -\frac{\partial \Omega}{\partial T} \to 0, \quad (4.4)
\]

for either sign of \((E_\gamma - \mu)\). Moreover, at finite temperatures, the summand of equation (4.3) given by

\[
k_B \left\{ \ln (1 + e^{-\beta x}) + \frac{x}{1 + e^x} \right\} > 0, \quad (4.5)
\]

is positive for all \(x\) in the range \([-\infty \to \infty]\), assuring the positivity of the entropy even with the negative component of the energy spectrum. (A plot of the function readily verifies this.)\(^{[17]}\)

Furthermore, we evaluate the entropy \(S_{\text{Deg}}\) for the Dichalcogenides in the approach to zero temperature in the degenerate regime: employing equations (3.8) and (4.1) we find (per unit area)

\[
S_{\text{Deg}} = k_B \frac{eB}{4\pi} \sum_{s = \pm 1} \sum_{s = \pm 1} \sum_{n = 0}^{\infty} \sum_{n = \pm}^{\infty} \left( 1 + (\pm' \frac{g}{\sqrt{z^2 + e^2_{n\pm}}} \right)
\]

\[
\times \left[ \ln (1 + \exp [(\mu - E_{i\pm} \pm' \sqrt{z^2 + e^2_{n\pm}}) \beta]) - \beta (\mu - E_{i\pm} \pm' \sqrt{z^2 + e^2_{n\pm}}) [1 + \exp(-[\mu - E_{i\pm} \pm' \sqrt{z^2 + e^2_{n\pm}} \beta])^{-1} \right]. \quad (4.6)
\]

It is readily verified (again) that the summand of equation (4.6) vanishes in the limit of zero temperature for energies above and below the Fermi level, including negative energies.

It should be noted that the entropy is important in the calculation of thermal properties. In particular, the specific heat at constant volume is given by \(^{[19]}\)

\[
C_v = T \left( \frac{\partial S}{\partial T} \right) |_V = -\beta \frac{\partial S}{\partial \beta}; \quad (4.7)
\]

Considering \(\partial S(\beta, \mu(\beta)) / \partial \beta\), we note that

\[
\frac{\partial S}{\partial \beta} = \frac{\partial S}{\partial \beta} \text{ explicit} + \frac{\partial S}{\partial \mu} \frac{\partial \mu}{\partial \beta} \quad (4.8)
\]

and

\[
\frac{\partial S}{\partial \mu} = -\frac{\partial}{\partial \mu} \left( \frac{\partial F}{\partial T} \right) = -\frac{\partial}{\partial T} \left( \frac{\partial F}{\partial \mu} \right) \equiv 0, \quad (4.9)
\]

so only the explicit dependence of \(S\) on temperature need be considered, with \(\mu\) held constant, in the differentiation. Employing equation (4.6) in the degenerate regime just above \(T^* = 0\), we have (per unit area)
\[ C_V = k_B \beta^2 \frac{e^B}{16\pi} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \sum_{j=-1}^{1} \sum_{l=0}^{\pm 1} \left( 1 \mp \beta' \right) \frac{g}{\sqrt{g^2 + \epsilon_{n+m}}^2} \times \left\{ \frac{|\mu - E_{n+m}|^2}{\cosh^2\left(|\mu - E_{n+m}|/\sqrt{g^2 + \epsilon_{n+m}}^2\right)} \right\} \]  

(4.10)

The specific heat is of particular interest as a measure of the ability of the material to assist in the management of dissipated heat, an issue of importance in electronic device operation and transport. Specific heat also plays an important role in a standard characterization technique employed to understand the underlying physics of the Dichalcogenides, as has been emphasized by Stewart [20] and Geballe’s group [21–25].

5. Discussion

The key thermodynamic function considered here in the presence of a quantizing magnetic field, the Grand Potential, \( \Omega = F - \mu N = -k_B T \ln Z \), has been examined in the degenerate statistical regime for the Group VI Dichalcogenides (which have both positive and negative unbounded energy branches) with an evaluation of its temperature dependence in the approach to the zero temperature limit. The results for the degenerate regime in equations (3.8, 9) include its zero—temperature contributions from energy levels \( E_i \), below the Fermi energy \( \mu > E_i \), (summand terms given by \( \eta_j(\mu - E_i) (\mu - E_i) \)) and finite temperature corrections from energy levels both above and below the Fermi energy (summand terms given by \( \beta^{-1} \ln(1 + \exp(-|\mu - E_i|/\beta)) \)). For \( E_i \) levels sufficiently removed from \( \mu \) so that \( |\mu - E_i|/\beta > 1 \), the temperature corrections are exponentially small \( \sim \beta^{-1} \exp(-|\mu - E_i|/\beta) \). However, if an energy level \( E_i \) is so close to \( \mu \) that \( |\mu - E_i|/\beta < 1 \), its contribution can be substantially larger than the zero—temperature counterpart in the ratio \( \sim 1/|\mu - E_i| \). The zero—temperature terms describe de Haas—van Alphen oscillatory phenomenology, in which abrupt changes in statistical thermodynamic (and other) functions are introduced when a varying magnetic field forces successive displaced/split Landau levels across the Fermi energy, inducing abrupt population/depopulation of states: This is represented mathematically by the activation/deactivation of a succession of associated Heaviside step functions, \( \eta_j(\mu - E_i) \), as the magnetic field changes. As indicated above, the ratio \( \sim 1/|\mu - E_i| \) provides a relative measure of the role of finite temperature in this process. Of course, the introduction of scattering/disorder will moderate this. In regard to the dHvA oscillatory phenomenology, it should be noted that the Dirac–like Landau energy levels are proportional to the square–roots of integers multiplying the magnetic field \( (\epsilon_{n+m} = \sqrt{(2n + 1 + \pm 1) \gamma^2 g \gamma^2}) \), so the simple periodicity of the dHvA oscillations of the nonrelativistic case no longer applies to the present ‘relativistic’ case involving more complex oscillatory behavior. Furthermore, it is important to bear in mind that the contributions of higher Landau–level–index–\( n \) terms in equations such as equations (3.8, 9) correspond to Landau eigenstates of correspondingly higher energies, and when those energies approach and exceed the limits of validity of the approximate low—energy ‘Dirac–like’ Hamiltonian under consideration (due to the curvature of the underlying band structure), such contributions must be discarded, constituting an effective ‘cut off’ terminating the ‘\( n \)’–series summation.

The remarks above also generally apply to \( \Delta M_{\text{Deg}}(T' = 0) \), the magnetic moment contribution at zero temperature, \( T' = 0 \) (equation (3.11)): the summand terms of \( \Delta M_{\text{Deg}}(T' = 0) \) have the form

\[ \Delta M_{\text{Deg}}(T' = 0) \sim \eta_j(\mu - E_i) (\mu - E_i) \]  

(5.1)

Again, de Haas–van Alphen oscillatory structure is induced by variation of the magnetic field in \( E_i \), causing abrupt activation/deactivation of the Heaviside step functions \( \eta_j(\mu - E_i) \) as successive energy levels \( E_i \), cross the Fermi energy \( \mu \); and these oscillations are not simply periodic because the Dirac Landau levels are proportional to the square–roots of integer multiples of the magnetic field \( B \). Our dHvA results may be useful in the interpretation of magnetic field experiments on the Dichalcogenides to help identify physical parameters such as \( E_i, g, \gamma \), etc.

On the other hand, finite temperature contributions involve all Landau levels, not just those crossing the Fermi energy (equation (3.12)), where the summand has the form

\[ \Delta M_{\text{Deg}}(T' > 0) \sim e^{-|\mu - E_i|/\beta} \left( \frac{1}{\beta} \mp \beta' \right) \frac{e^{\gamma^2}}{\sqrt{g^2 + \epsilon_{n+m}^2}} \]  

(5.2)

For energy levels \( E_i \), that are well separated from \( \mu \) (above or below) such that \( |\mu - E_i|/\beta > 1 \), we have \( \Delta M_{\text{Deg}}(T > 0) \sim \left( \frac{1}{\beta} \mp \beta' \right) e^{-|\mu - E_i|/\beta} \) is exponentially small. However, for a level \( E_i \) crossing the Fermi energy, \( |\mu - E_i|/\beta < 1 \), we have
\[ \Delta M_{\text{Deg}}(T' > 0) \sim \frac{1}{\beta} \pi' \epsilon_j, \] (5.3)

This is (approximately) the only temperature dependent contribution for levels near \( \mu \) and it is competitive with the zero temperature contribution

\[ \Delta M_{\text{Deg}}(T' = 0) \sim |-\mu \partial n / \partial B| \text{ in the degenerate regime (equation (3.14))}, \]

Examining the magnetic moment contributions from \(-\mu \partial n / \partial B\) in the degenerate regime (equation (3.14)), we note that the summand terms have the form

\[ -\left( \frac{\partial n}{\partial B} \right)_{\text{Deg}, T=0} \sim \eta_+ (\mu - E_\gamma) \mu - \delta (\mu - E_\gamma) \epsilon_e + \mu, \] (5.5)

which are competitive with the corresponding terms of \( \Delta M_{\text{Deg}}(T' = 0) \) in equation (3.11), and exhibit dHvA resonant behavior at \( \mu = E_\gamma \) (again, moderated by finite temperature as one can easily see from equation (3.12), as well as scattering/disorder and other interactions).

We have addressed the salient features of the entropy of systems having an unbounded negative component of their energy spectrum (as well as a positive component), verifying that the entropy of such systems is always positive and vanishes at \( T' = 0 \), notwithstanding the negative energy component.

Our result for entropy of the Dichalcogenides in the degenerate regime is devoid of de Haas–van Alphen oscillatory features, as one should expect from the vanishing temperature derivative of the leading term of \( \Omega = F - \mu N \) which is the sole source of dHvA behavior, but is independent of temperature. The approach to zero temperature is shown in \( S_{\text{Deg}} \) of equation (4.6), and for energies with \( |\mu - E_\gamma| \beta > 1 \), its summand terms exhibit an exponential fall–off to zero, as expected for both positive and negative energies \( E_\gamma \). For energies with \( |\mu - E_\gamma| \beta < 1 \), the summand terms have the form \( S_{\text{Deg}} \sim \ln 2 \).

The importance of the specific heat as a standard characterization technique to understand the underlying physics of the Dichalcogenides has been emphasized by Stewart \cite{25} and Geballe’s group \cite{26,27,28}; and our specific heat results in equations (4.10) can be employed to interpret relevant data for this purpose. Of course, our results for de Haas–van Alphen oscillations in the magnetic moment can also be employed to characterize the Dichalcogenide material parameters.

In conclusion, it is appropriate to point out that this analysis of Landau quantization effects in the statistical thermodynamics of Dirac materials, albeit ‘relativistic,’ is subject to the Bohr–van Leeuven theorem \cite{26,27,28}. This is to say that as the discrete Landau levels approach one another in a decreasing magnetic field, they experience a kind of phase–averaging and their low field limit is devoid of dHvA diamagnetic oscillatory behavior in the magnetic moment and related statistical thermodynamic functions. This fact is associated with the Hamiltonian replacement \( \vec{p} \rightarrow \vec{p} - e \vec{A} / c \), from which the magnetic field can be eliminated by transformation in classical statistical functions as Landau level separation vanishes, leaving only the spin terms intact in the magnetic moment of the Dirac materials, including the Dichalcogenides (as well as in the more usual ‘non–relativistic’ materials).

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Note Added in Proof

After this work was completed, we became aware of other related work by Sharapov, Gusynin, and Beck \cite{29,30}.

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