Dispersion relations for the quadratic Zeeman effect in heliumlike atoms

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The analyticity properties and the asymptotic behavior of the quadratic Zeeman energy shifts $\delta E$ for an atom are analyzed, leading to once-subtracted dispersion relations for the energy shifts. In conjunction with the WKB expression for $\text{Im}\delta E$ in the weak-field limit and perturbation expressions for the susceptibility and the strong-field limit of $\text{Im}\delta E$, these dispersion relations allow us to obtain (i) the large-$n$ behavior of the ratios of the expansion coefficients of the perturbation series, and (ii) the energy shifts for the symmetric ground state of $\text{He}$ and $\text{Li}^+$. 

I. INTRODUCTION

The quadratic Zeeman effect, though very small for laboratory magnetic fields, can be important in astrophysics, where atoms are acted on by immensely large magnetic fields.\(^{1}\) It is also expected to be important for certain electronic states of donor impurities\(^{2}\) and excitons\(^{3}\) in semiconductors. Apart from this practical importance, the effect is of considerable theoretical interest as an example of a perturbation yielding a divergent series which, however, may be asymptotic. Consequently, one takes recourse to nonperturbative techniques for the analysis of the quadratic Zeeman effect.

The energy shift in the hydrogenlike atoms due to the quadratic Zeeman interaction has attracted a great deal of attention because of the relative simplicity of its Hamiltonian. In addition to the rigorous mathematical considerations\(^{4}\) which have led to some limited results, it has been analyzed by the variational methods,\(^{5}\) the truncated basis approach,\(^{6}\) and the summability procedure of Pade approximants.\(^{7}\) It has also been analyzed by using dispersion relations\(^{8\text{-}10}\) leading to high-order expansion coefficients of the perturbation series and to an approximate expression for the energy shift in the ground state for the entire range of the magnetic field. In contrast, the corresponding problem for the heliumlike atoms has been analyzed only in terms of variational methods\(^{11,12}\) and Hartree-Fock wave functions.\(^{13}\) There has also been derived\(^{14}\) a rigorous expression for the symmetric ground state for large magnetic fields and for large nuclear charge. However, there has not been any significant effort to provide a unified description of the behavior of the energy shift for the heliumlike atoms over the entire range of the magnetic field.

In this paper, we suggest that dispersion relations are a useful framework for the analysis of the quadratic Zeeman energy shift for the heliumlike atoms, and possibly for any arbitrary atom as well. They not only allow a compact representation of the analyticity properties but also provide a practical tool for calculating the energy shift for the heliumlike atoms. This is especially welcome in view of the fact that the three-body complications make any detailed calculations for helium very difficult.

We first discuss, from general considerations, the nature of singularities of the quadratic Zeeman energy shift in the heliumlike atoms. It is shown that the energy shift as a function of $\gamma = (1/c^2)H^2$ satisfies the Herglotz property, and hence has no poles or algebraic branch point singularities with negative powers in the complex cut-plane $-\pi < \phi y < \pi$. We then assume that the milder singularities are absent or unimportant. This assumption leads us to dispersion relations for the energy shift. In the second part of the paper we discuss the weak- and strong-field limits of the energy shift for the heliumlike atoms, the large-$n$ behavior of the coefficients of $\gamma^s$ in the perturbation series for the energy shift, and the continuation of the energy shift on to the second sheet near $\gamma = 0$. Some of these results are also applicable to an arbitrary state of any atom. In the second part of the paper, we parametrize the dispersion integrands for the heliumlike atoms, so as to be consistent with the required weak- and strong-field limits. The dispersion relations then provide a framework which allows us to calculate the energy shift in the symmetric ground state of helium and $\text{Li}^+$ over a wide range of the magnetic field. The predictions for the energy shift are in good agreement with the strong-field results of Mueller et al.,\(^{15}\) and are expected to be valid over the intermediate and weak-field regions as well.

II. GENERAL CONSIDERATIONS

The Hamiltonian for the quadratic Zeeman effect in the heliumlike atoms is

$$H = \frac{1}{2}(p_1^2 + p_2^2) - Z \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} + \frac{\gamma}{8} (p_1^2 + p_2^2),$$

(1)
\[ \rho_i^2 = x_i^2 + y_i^2, \]  
where \( \gamma = (1/c^2)H \) and \( \gamma = 1 \) corresponds to a field strength of \( 2.35 \times 10^9 \) gauss. We can deduce some properties of the energy levels from general considerations of this Hamiltonian. Most of the following arguments are based on Simon's analysis\(^1\) for the anharmonic oscillator.

### A. Herglotz property

The asymptotic behavior of the wave function is given by

\[ \psi \sim \exp \left[ -\frac{1}{2} \gamma^{1/2} (\rho_1^2 + \rho_2^2) f(\tau_1, \tau_2) \right], \tag{3} \]

where \( f \) is polynomially bounded. For obtaining the Herglotz property, we start with the relation

\[ \langle \phi | H | \phi \rangle = E(\phi \langle | \phi \rangle). \tag{4} \]

On substituting (1) for the Hamiltonian, and taking imaginary parts, one obtains

\[ \text{Im} E(\gamma) = \frac{1}{2} \langle \phi | (\rho_1^2 + \rho_2^2) \phi \rangle \tag{5} \]

From the asymptotic behavior (3), it follows that for \( -\pi \leq \phi \leq \pi \) but \( \text{Im} \gamma \neq 0 \),

\[ \frac{\text{Im} E(\gamma)}{\text{Im} \gamma} > 0 \tag{6} \]

and is finite. This Herglotz property immediately implies an important result\(^2\) that \( E(\gamma) \) has no poles in the complex cut-plane \(-\pi < \phi \gamma < \pi\), since a pole would dominate in its neighborhood and can have any phase, depending on the direction of approach to the pole. Similar arguments also exclude algebraic branch point singularities with negative powers.

### B. Real positive \( \gamma \)

For real positive \( \gamma \), one has from the Hellmann-Feynman theorem

\[ \frac{\partial E(\gamma)}{\partial \gamma} = \frac{1}{2} \langle \phi | (\rho_1^2 + \rho_2^2) \langle \phi | \rangle \tag{7} \]

This, in view of (3), is real, finite, and positive,\(^3\) which implies that \( E(\gamma) \) is a real, monotonically increasing function of \( \gamma \) in the physical region.

### C. Scale transformations

Consider a Symanzik scale transformation\(^4\)

\[ \tau_i = \lambda^{-2} \tau_i, \quad \rho_i = \lambda \rho_i, \tag{8} \]

which takes Hamiltonian (1) into

\[ H' = \lambda^2 \left[ \frac{1}{2} (\rho_1^2 + \rho_2^2) - \frac{1}{\lambda} \left( \frac{Z}{\tau_1^2} + \frac{Z}{\tau_2^2} - \frac{1}{\tau_{12}^2} \right) + \frac{\gamma}{8\lambda^4} (\rho_1^2 + \rho_2^2) \right]. \tag{9} \]

Since the scale transformation is unitarily implementable, \( H \) and \( H' \) have the same eigenvalues. Regarding \( E \) as a function of the coefficients of \( 1/\tau_{12} \) and \( \frac{1}{2} (\rho_1^2 + \rho_2^2) \), one obtains

\[ E(1, \gamma) = \lambda^2 E \left( \frac{1}{\lambda}, \frac{\gamma}{\lambda^4} \right). \tag{10} \]

In particular, if one takes \( \lambda = (\gamma/4)^{1/4} \) and lets \( \gamma \to \infty \), we have the asymptotic behavior

\[ E(1, \gamma) = \left( \frac{\gamma}{4} \right)^{1/2} E \left( \left( \frac{\gamma}{4} \right)^{-1/4}, 4 \right) \tag{11} \]

\[ \rightarrow \gamma^{1/2}. \tag{12} \]

This is a direct extension of the result of Avron et al.\(^5\) for the one-electron atom to the two-electron atom.

### D. The point \( \gamma = 0 \)

One can use relation (11) to show that \( \gamma = 0 \) is a singular point of \( E(1, \gamma) \) or equivalently, of \( E(\gamma) \). Suppose \( \gamma = 0 \) is a nonsingular point. We start\(^6\) from large positive \( \gamma \), move along the real axis towards zero, and after encircling the origin, go back to infinity. If \( \gamma = 0 \) is a nonsingular point, \( E(1, \gamma) \) must have the same value at the beginning and at the end. However, as we go around the origin, \( \gamma \) acquires a phase of \( 2\pi \), so that Eq. (11) leads to

\[ \left( \frac{\gamma}{4} \right)^{1/2} E(0, 4) = -\left( \frac{\gamma}{4} \right)^{1/2} E(0, 4), \quad \gamma \to \infty. \tag{13} \]

This is contradictory, since \( E(0, 4) \) is positive definite. As this relation follows from the assumption that \( \gamma = 0 \) is a nonsingular point, we conclude that \( \gamma = 0 \) is a singular point of \( E(\gamma) \), analogous to the similar result for the hydrogen atom.\(^4,10\)

It is obvious that the results of this section can be easily extended to the quadratic Zeeman effect in any atom, and are similar to the corresponding properties for the energy levels in the hydrogen atom.\(^4,10\)

### III. Dispersion Relations

In the previous section we showed that \( E(\gamma) \) has no poles or branch-point singularities with negative powers in the complex cut-plane \(-\pi < \phi \gamma < \pi\), but is singular at \( \gamma = 0 \). We are unable to eliminate the possibility of the existence of milder
singularities such as logarithmic singularities or branch-point singularities with positive powers. This is a general difficulty which remains unresolved even in the case of the anharmonic oscillator. From a practical point of view, we will assume that these singularities are either absent or unimportant. Since \( E(\gamma) \sim (\gamma + \delta)^{1/2} \) for \( \gamma \to \infty \), one can then write one-subtracted dispersion relations for \( E(\gamma) \):

\[
E(\gamma) = E(0) + \gamma \int_{-\infty}^{0} \frac{\text{Im}E(\gamma')}{\gamma'(\gamma' - \gamma)} d\gamma',
\]

where \( \text{Im}E(\gamma') \) is for \( \gamma' \to 0 \). Furthermore, one may write

\[
E(\gamma) = E(0) + \sum_{n=1}^{\infty} A_{n} \gamma^{n},
\]

where \( A_{n} \) are given by

\[
A_{n} = \frac{1}{\pi} \int_{-\infty}^{0} \frac{\text{Im}E(\gamma')}{\gamma'(\gamma' - \gamma)} d\gamma',
\]

assuming that the integrals exist. These relations are powerful relations and can yield useful results for \( E(\gamma) \).

For evaluating the dispersion relations, we require information \( \text{Im}E(\gamma) \) for negative \( \gamma \), which, in general, is not readily available. However, the symmetric ground state of helium has several special properties which allows us to analyze the dispersion relations for the energy level in some details.

### A. Relation to the hydrogen atom

It is known that the ground state of helium is well simulated by an independent particle model with a screened nucleus. It is therefore convenient to write

\[
H = H_{0} + H_{1},
\]

with

\[
H_{0} = \frac{1}{2}(p_{r}^{2} + p_{\theta}^{2}) - Z' \left( \frac{1}{r_{1}} + \frac{1}{r_{2}} \right) + \frac{\gamma}{8} (\rho_{1}^{2} + \rho_{2}^{2}),
\]

\[
H_{1} = \frac{1}{r_{12}} - (Z - Z') \left( \frac{1}{r_{1}} + \frac{1}{r_{2}} \right).
\]

The choice of the value of \( Z' \) will be guided by the requirement that the contribution of \( H_{1} \) to the energy levels should be small, so that we may evaluate its effect approximately. For this we note that \( Z' \) has a variational value of \( Z = \frac{1}{2} \) for exponential wave functions in the absence of the magnetic field. The corresponding variational value of \( Z' \) for \( \gamma \to \infty \) has been shown to be \( Z = \frac{1}{2} \). We take \( Z' = Z = \frac{1}{2} \), which is appropriate for small fields. While it is not equally satisfactory for large fields, we do include the perturbative corrections due to \( H_{1} \) in this limit.

If \( H_{0} \) is subjected to scale transformation (8) with \( \lambda = Z' \), one gets

\[
H_{0}' = Z'^{2} \left[ \frac{1}{2}(p_{1}^{2} + p_{2}^{2}) - \left( \frac{1}{r_{1}} + \frac{1}{r_{2}} \right) + \frac{\gamma}{8Z'^{2}} (\rho_{1}^{2} + \rho_{2}^{2}) \right],
\]

which is related to the hydrogenic Hamiltonian with \( \gamma_{\text{eff}} = \gamma/Z'^{2} \). One can therefore write

\[
\delta E(\gamma) = 2Z'^{2}\delta E_{H}(\gamma/Z'^{2}) + f(\gamma),
\]

where \( \delta E \) is the shift in the symmetric ground state energy of the heliumlike atom, \( \delta E_{H} \) is the corresponding shift for the hydrogen atom, and \( f \) is the correction due to \( H_{1} \), which may be expected to be small. Moreover, since \( \delta E_{H}(\gamma) \) satisfies the same dispersion relations as \( \delta E(\gamma) \), \( f(\gamma) \) also satisfies similar dispersion relations, so that we have

\[
\delta E(\gamma) = 2Z'^{2}\delta E_{H}(\gamma/Z'^{2}) + \frac{\gamma}{\pi} \int_{-\infty}^{0} \frac{\text{Im}E'(\gamma')}{\gamma'(\gamma' - \gamma)} d\gamma'.
\]

### B. Susceptibility

Atomic susceptibility

\[
\chi = 2 \frac{\partial E}{\partial \gamma} \quad \text{at} \quad \gamma = 0
\]

provides a constraint on the dispersion integral in Eq. (22). From the known perturbation expansion for \( \delta E_{H} \), one gets

\[
\chi = \frac{1}{Z'^{2}} + \frac{2}{\pi} \int_{-\infty}^{0} \frac{\text{Im}E'(\gamma')}{\gamma'^{2}} d\gamma'.
\]

It is possible to get a fairly good approximation for \( \chi \) by treating \( H_{0} \) as the unperturbed Hamiltonian and \( H_{1} \) as a perturbation. For example, the first order perturbation calculation gives

\[
\chi = \frac{1}{Z'^{2}} + \frac{11}{64} \left( \frac{1}{Z'^{3}} \right).
\]

For helium, this expression has a value of 0.387 while the experimental value of \( \chi \) is 0.394. We therefore take

\[
\frac{1}{\pi} \int_{-\infty}^{0} \frac{\text{Im}E'(\gamma')}{\gamma'^{2}} d\gamma' = \frac{1}{Z'^{2}}
\]

which gives the correct experimental value for the susceptibility of helium. This relation gives a useful constraint on \( \text{Im}E(\gamma) \).

### C. \text{Im}E(\gamma) for \( \gamma \to 0 \)

One can deduce the field dependence of the decay probability or \( \text{Im}E(\gamma) \) for \( \gamma \to 0 \). For any state of an
atom, in terms of the ionization energy $E_i$ of the state, nuclear charge $Z$, and the total number of electrons $n_{el}$ in the atom. This is done by noting that the electron which escapes from the atom in the presence of a weak repulsive simple harmonic potential comes out with energy $(-E_i)$ and sees a charge

$$\alpha = Z - n_{el} + 1$$

when it is at a large distance from the atom.

Therefore, the wave function of the escaping electron is of the form

$$\psi = Y_i^\dagger(\theta, \phi) r^{(\alpha - 1)/2} \exp(-\rho r)$$

for $1 < r < |\gamma|^{-1/3}$,

where $\rho = (2E_i)^{1/2}$. This wave function has an integral representation

$$\psi = \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y e^{ik_x x + ik_y y}$$

$$\times h(k_x, k_y) \left( \frac{\epsilon}{4 \kappa^2} \right)^{1/2}$$

$$\times \exp \left( -\frac{(\alpha - 1/2)\rho}{\kappa} \right)$$

(32)

where

$$h(k_x, k_y) = \begin{cases} 1 & \text{for } (l+m) \text{ even} \\ k_y & \text{for } (l+m) \text{ odd} \end{cases}$$

(33)

which is obtained by carrying out the angular integration in (29). This is a superposition of the functions

$$\phi_k(\xi, \rho) = e^{i\xi x} \rho^{(\alpha/2 - 1/2)} e^{i\kappa(\varepsilon(\alpha/2) + 1/2)z}$$

(34)

which are separable solutions of the Schrödinger equation (31) in the important neighborhood of $k^2 + \rho^2 = 0$. They can be continued into the region $\rho > |\gamma|^{-1/3}$ by using the WKB approximation:

$$\phi_k(\xi, \rho) = \phi_k(\xi, \rho_0) \left( \frac{\partial_k k_x}{\rho} \right)^{1/2} \left( k_x^2 + \frac{2\alpha}{\rho} + \frac{1}{4} |\gamma| \rho \right)^{-1/4}$$

$$\times \exp \left[ i \int_{\rho_0}^{\rho} \left( k_x^2 + \frac{2\alpha}{\rho} + \frac{1}{4} |\gamma| \rho \right)^{1/2} d\rho \right]$$

(35)

for $\rho > 1$, where $1 < \rho_0 < |\gamma|^{-1/3}$. The integration in (35) can be carried out for $\rho > 1$, leading to

$$\psi = \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \frac{k_x \rho^{1/2} \delta_k}{\rho_0}$$

$$\times \exp \left[ i \int_{\rho_0}^{\rho} \left( k_x^2 + \frac{2\alpha}{\rho} + \frac{1}{4} |\gamma| \rho \right)^{1/2} d\rho \right]$$

(36)

where

$$f(k_x, k_y) = \ln \left( \frac{k_x^2 + \rho^2 + \frac{1}{2} |\gamma| \rho^2}{k_x^2 + \rho^2} \right)$$

(37)

and $\epsilon = \frac{1}{4} |\gamma|$. The integrals in (36) are evaluated by the saddle point method. For small $\epsilon$, the variation in the integrand is primarily due to $f(k_x, k_y)$. The saddle point is therefore located by requiring

$$\frac{\partial f}{\partial k_x} = \frac{\partial f}{\partial k_y} = 0,$$

(38)

and is given by

$$k_x = \frac{\varepsilon^{1/2}}{\Lambda} \left( 1 + \frac{\ln \rho}{\Lambda} + \frac{i\pi}{2\Lambda} \right),$$

$$k_y = \frac{2\varepsilon^{1/2}}{\Lambda} \left( 1 + \frac{\ln \rho}{\Lambda} + \frac{i\pi}{2\Lambda} \right),$$

(39)

where $\Lambda = \ln(2\varepsilon^{1/2}/\rho)$. Expanding $f(k_x, k_y)$ about the point $(\hat{k}_x, \hat{k}_y)$ and carrying out the Gaussian integrals, we finally get

$$|\psi| = \frac{h(\varepsilon^{1/2}/\Lambda)}{\rho^{1/2} \Lambda^{1/2}} \left( \frac{\rho}{\rho} \right)^{-1/2}$$

$$\times \exp \left( -\frac{\pi \rho^2}{4\varepsilon^{1/2}} - \frac{\pi \varepsilon^{1/2}\rho^2}{4\Lambda^2} \right),$$

(40)

where the function $h(\varepsilon^{1/2}/\Lambda)$ is defined in Eq. (33). The decay probability and Im$E(\gamma)$ are given by

$$W = 2 \text{Im} E(\gamma)$$

$$= 2\pi \int |\psi|^2 \rho^2 d\xi.$$  

(41)
The integration in Eq. (41) with \( \psi \) from Eq. (40) leads to
\[
\text{Im}E(y) - \gamma^{1/4}e^{-(2E_{\text{ion}})1/2} \exp(-\pi E_{\text{ion}}^2 |y|^{-1/2}) \text{ for } (l+m) \text{ even,}
\]
\[
\text{Im}E(y) - \gamma^{3/4} \exp(-\pi Z^2 |y|^{-1/2}) \text{ for } (l+m) \text{ odd, for } \gamma = 0_+.
\]
(42)

where \( p^2 = 2E, \ E \) being the ionization energy of the level, and \( \alpha = (\gamma - n_\alpha + 1) \) is the charge seen by the escaping electron. This is a general result and applies to any state of any atom, for which there is no \( l \) degeneracy. It also agrees with the results obtained by Avron for the special case of the hydrogen atom.

It is interesting to observe that the field dependence of \( \text{Im}E(y) \) and the decay width, in the weak-field limit, is determined only by the ionization energy of the electron and the charge seen by the escaping electron. The constant factor in general depends upon the details of the state. It has been discussed for the special case of the hydrogen atom by Avron. We note that our result for the field dependence of \( \text{Im}E(y) \) agrees with the known results for the hydrogen atom for which \( \rho = 1/n \) with \( n \) being the principal quantum number, and \( \alpha = 1 \).

For the ground state of the helium atom, our result is
\[
\text{Im}E(y) - \gamma^{1/4}e^{-(2E_{\text{ion}})1/2} \exp(-2\pi E_{\text{ion}}^2 |y|^{-1/2})
\]
for \( \gamma = 0_+ \). (43)

where \( E_{\text{ion}} \) is the ionization energy for the helium atom. One also has the result
\[
\text{Im}E(y) - \gamma^{3/4} \exp(-\pi Z^2 |y|^{-1/2})
\]
for \( \gamma = 0_+ \). (44)

However,
\[
E_{\text{ion}} = Z^2 - \frac{Z^2}{2}
\]
\[
< \frac{3}{2} Z^2
\]
(45)

so that \( \text{Im}E(y)/Z^4 \) is subdominant for \( \gamma = 0_+ \). We therefore conclude from (22) and (43) that
\[
\text{Im}E(y) - \gamma^{3/4}e^{-(2E_{\text{ion}})1/2} \exp(-2\pi E_{\text{ion}}^2 |y|^{-1/2})
\]
for \( \gamma = 0_+ \). (46)

D. Strong-field limit

For evaluating the strong-field limit of the \( E(y) \), we reduce the problem to that of one-dimensional motion in a weak potential. For this we consider the scale-transformed Hamiltonian with \( \lambda = (\gamma/4)^{1/4} \), which can be written as
\[
\left(\frac{4}{\gamma}\right)^{1/2} H' = h_0' + h_1',
\]
(47)

\[
h_0' = \frac{1}{2}(p_1^2 + p_2^2) + \frac{1}{2}(p_1^2 + p_2^2) - Z' \left(\frac{4}{\gamma}\right)^{1/4} \left(\frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right),
\]
(48)

\[
h_1' = \left(\frac{4}{\gamma}\right)^{1/4} \left[\frac{1}{\gamma_1} - (Z - Z') \left(\frac{1}{\gamma_1} + \frac{1}{\gamma_2}\right)\right].
\]
(49)

The strong-field behavior of the eigenvalue of \( h_0' \) has been found by Avron to be
\[
\epsilon_0' - 2 - 8(\gamma)^{1/2} Z^2 \left[\ln \left(\frac{\gamma}{4}\right)^{1/2} - \ln \left(\frac{\gamma_{1/2}}{4}\right)^{3}\right]
\]
for \( \gamma - \infty \). (50)

The first-order contribution of \( h_1' \) to the energy can be obtained by noting that the approximate eigenfunctions of (48) can be written as
\[
\psi = \phi (\vec{r}_1) \phi (\vec{r}_2),
\]
(51)

\[
\phi (\vec{r}_1) = \left(\frac{2 - \epsilon_0'}{2} - \mathcal{E}_{1/2} \right) e^{-\mathcal{E}_{1/2} r_1}.
\]
(52)

Then the expectation value of \( h_1' \) in the strong-field limit comes out to be
\[
\langle h_1' \rangle = \left(\frac{4}{\gamma}\right)^{1/4} \left(2 - \epsilon_0'\right)^{1/2} \ln (2 - \epsilon_0') \left[1 - 4(Z - Z')\right],
\]
(53)

so that we have for \( E(y) \) in the strong-field limit,
\[
E(y) - \gamma^{1/2} - 4(Z^2 + \frac{1}{\gamma} Z') \left[ \frac{1}{2} \ln \left(\frac{\gamma_{1/2}}{4}\right) - \ln \left(\frac{\gamma_{1/2}}{4}\right) \right]^2
\]
for \( \gamma - \infty \), (54)

where we have used \( Z - Z' = \frac{1}{10} \). Now, since the contribution of \( h_0' \) corresponds to the contribution of \( \epsilon E_{\text{ion}} \) in (21), one has
\[
f(y) = - \frac{1}{2} Z \left[ \frac{1}{2} \ln \left(\frac{\gamma_{1/2}}{4}\right) - \ln \left(\frac{\gamma_{1/2}}{4}\right) \right]^2
\]
for \( \gamma - \infty \). (55)

Continuing this to \( \gamma - \infty \), we finally get for the leading behavior,
\[
f(y) = - \frac{\pi}{4} Z \left[ \frac{1}{2} \ln \left(\frac{\gamma_{1/2}}{4}\right) - \ln \left(\frac{\gamma_{1/2}}{4}\right) \right]
\]
for \( \gamma - \infty \). (56)

IV. APPLICATIONS

In this section we show that the dispersion relations (14) and the information about \( \text{Im}E(y) \) in the weak- and strong-field limits, can be used to predict the behavior of the energy shifts. We
first discuss the large-\(n\) behavior of the coefficient of \(\gamma^n\) in the perturbation series.

### A. Asymptotic series

It is observed that the major contribution to the integral (16) for \(A_n\) for \(n \to \infty\) comes from the small-\(\gamma\) region where we can use (42). Let

\[
\text{Im}E(\gamma)\gamma D|\gamma|^2 \exp\left(-\frac{2\pi E}{|\gamma|^2/2}\right) \quad \text{for} \quad \gamma \to 0, 
\]

where \(a\) can be obtained from Eq. (42) and \(D\) is an unknown constant. This expression leads to

\[
A_n = \frac{D}{\bar{\gamma}} \int_{-\infty}^{0} \frac{\exp\left(-\frac{2\pi E}{|\gamma|^2/2}\right)}{(|\gamma|^2/2)^{s+1}} |\gamma|^2 d\bar{\gamma}
\]

\[
= (-1)^{s+1} \frac{2D}{\bar{\gamma}} \left(2\pi E\right)^{s+1/2} \Gamma(2n-2s) \quad \text{for} \quad n \to \infty,
\]

from which we deduce that

\[
\frac{A_{s+1}}{A_s} = -\frac{m^2}{\pi^2 E^2} + \text{O}(n) \quad \text{for} \quad n \to \infty.
\]

These are very general results and are valid for the quadratic Zeeman energy shift in any atom. They are implied by the singular behavior at \(\gamma = 0\) and depend only on the binding energy of the state and not on the details of the interaction. In particular, they can be shown to be valid for the hydrogen atom for which detailed information is available.\(^5\)\(^-\)\(^9\)

A similar analysis can be carried out for the Stark effect as well. Corresponding to Eq. (42), we have for nondegenerate states,

\[
\text{Im}\delta E(\epsilon) = F\epsilon^2 \exp\left(-\frac{2(2E)^{3/2}}{3\epsilon}\right) \quad \text{for} \quad \epsilon \to 0,
\]

where \(\epsilon\) is the strength of the electric field \(\epsilon = 1 + |m| - 2\alpha(2E)^{-1/2}\), \(E\) is the ionization energy of the state, \(m\) is the magnetic quantum number, \(\alpha\) is defined in Eq. (42), and \(F\) is an unknown constant. Using this expression in the dispersion relations\(^7\)\(^-\)\(^9\) leads to

\[
\text{Im}\gamma = \left[c_0 |\gamma|^{1/2} \left|2E_{\text{ion}}^{-1/2}\right| + c_2\right] \quad \text{for} \quad \gamma \to 0,
\]

where \(f = |\gamma|^{1/2} / (|\gamma|^{1/2} + 2c_2)\). This expression is consistent with the weak-field limit (46), and the strong-field limit (56). The constants \(c\) and \(c_2\) are taken to have the values

\[
c = 1.03, \quad c_2 = 17.73,
\]

from which we get

\[
a_n = \frac{2F}{\pi} \left(\frac{2(2E)^{3/2}}{3}\right)^{n+2} \Gamma(2n-2) \quad \text{for} \quad n \to \infty.
\]

These results are valid for any nondegenerate state of an atom in a uniform electric field. For the hydrogen atom, degeneracy mixing gives a different asymptotic behavior for \(\theta \sim \pi\) from that at other angles, which introduces an extra factor of \(\epsilon^{2n}\) in Eq. (60), thereby effectively increasing \(b\) by \(2n_1\), where \(n_1\) is the first parabolic quantum number. The expression then agrees with the hydrogenic expression obtained earlier.\(^8\)

### B. Continuation on to the second sheet

For continuation on to the second sheet, for \(\gamma \to 0\), we can use dispersion relations (14) with \(\text{Im}E(\gamma)\) given in the weak-field limit by Eq. (57):

\[
E(\gamma) = E(0) + \frac{\gamma}{\pi} D \int_{-\infty}^{0} \frac{(-\gamma')^2 \exp\left(-2\pi E(\gamma')^{-1/2}\right)}{\gamma' (\gamma' - \gamma)} d\gamma'.
\]

As \(\gamma\) encircles the origin and goes on to the second sheet, we distort the path of integration. Because of the form of the integrand, the distortion is allowed for \(\gamma \to 0\) only if \(\text{Re}(\gamma)^{1/2} > 0\). This means that after encircling the origin we come across singularities at \(\text{arg}(\gamma) = 2\pi\). The result indicates that for any atom \(\gamma = 0\) is a limit point of singularities on the second sheet which have a limiting phase of \(2\pi\).

### C. Energy shifts for the symmetric ground state of helium

For a quantitative prediction of the energy shifts from dispersion relations (22), we require an expression for \(\text{Im}f(\gamma)\) which is valid over the range \(\gamma = -\infty\) to 0. For this, we choose a parametric form

\[
\text{Im}f(\gamma) = \left[c_0 |\gamma|^{1/2} \left|2E_{\text{ion}}^{-1/2}\right| + c_2\right] \quad \text{for} \quad \gamma \to -\infty,
\]

so that the strong-field limit of (64) for \(E_{\text{ion}} = \frac{3}{2}\), has the same form as that of the leading terms in the hydrogenic expression in Ref. 10. Finally, the constant \(c_0\) is determined by the constraint (26) from susceptibility, and has the values

\[
c_0 = 3.29 \quad \text{for He}, \quad c_0 = 32.0 \quad \text{for Li}^+.
\]
With these values of the constants, we have carried out the integration in (22) and together with the values of $\delta E_e$ determined earlier,\textsuperscript{12} we predict energy shifts for the symmetric ground state of He and Li'. The calculated values are given in Table I, along with the predictions of Mueller et al.,\textsuperscript{12} for strong fields. The agreement between the two sets of values is quite good except for small values of $\gamma$ at which the strong-field calculations of Mueller et al. are not expected to be reliable. It is worth noting that the contribution of $f(y)$ to $[\gamma^{1/2} - \delta E(y)]$ is quite small over the entire range of $\gamma$, always less than 15%, which justifies our perturbative treatment of $f(y)$. We have not considered the case of $H'$ for which the perturbative analysis is not expected to be particularly useful.

V. SUMMARY

We have discussed the nature of the singularities of the quadratic Zeeman energy shift for an arbitrary state of any atom, from general considerations. The energy shift as a function of $\gamma = H^2/c^3$ satisfies the Herglotz property and hence has no poles or algebraic branch-point singularities with negative powers in the complex cut-plane $-\pi < \text{arg} y < \pi$. Assumption of the absence of milder singularities leads to once-subtracted dispersion relations.

The WKBo method which is applicable for weak fields has been used to deduce the field dependence of $\text{Im}E(y)$ in the weak-field limit $\gamma \rightarrow 0$. This dependence allows us to obtain the ratio of $A_{s+1}/A_s$, where $A_s$ are the coefficients in the perturbation series for $E(y)$, in terms of only the ionization energy of the state. The importance of these results lies in their complete generality. We have indicated that similar results are valid for the Stark energy shift also.

The special case of the two-electron atom allows us to separate out the energy shift of an electron moving in an effective screened Coulomb potential and treat the remaining part perturbatively. This leads to a reasonable parametrization of the dispersion integral, and hence to quantitative predictions of the energy shift for He and Li', which are in good agreement with the variational calculations. These results should be viewed with the background in which the three-body complications severely constrain any systematic analysis of heliumlike atoms apart from the variational analysis.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$\gamma^{1/2}$ & $A$ & $A_s$ & $B$ & $B_s$ \\
\hline
0.1 & 0.09804 & 0.09927 \\
0.2 & 0.19220 & 0.19710 \\
0.3 & 0.2826 & 0.2934 \\
0.4 & 0.3693 & 0.3883 \\
0.5 & 0.4527 & 0.4818 \\
0.6 & 0.6100 & 0.6644 \\
0.7 & 0.825 & 0.9280 \\
0.8 & 1.417 & 1.725 \\
0.9 & 1.89 & 2.41 \\
1.0 & 2.38 & 3.22 & 0.3 \\
1.1 & 4.255 & 6.16 & 5.15 & 9.26 & 7.3 \\
1.2 & 42.55 & 8.74 & 7.47 & 13.69 & 11.6 \\
1.3 & 212.75 & 16.45 & 15.06 & 29.3 & 26.5 \\
1.4 & 425.5 & 20.6 & 19.5 & 37.7 & 35.4 \\
1.5 & 2127.5 & 32.3 & 33.1 & 61.2 & 63.3 \\
1.6 & 4255 & 40.0 & 40.5 & 73.8 & 79.1 \\
1.7 & 21275 & 62.2 & 61.9 & 117.0 & 125.8 \\
\hline
\end{tabular}
\caption{Predictions of dispersion relations for $A = \gamma^{1/2} - \delta E_H$ and $B = \gamma^{1/2} - \delta E_L$, along with the corresponding predictions $A_s$ and $B_s$ of Mueller et al. (Ref. 12) for He and Li', respectively.}
\end{table}

\bibitem{7} A. Galindo and F. Pascual, Nuovo Cimento 34B, 155 (1976).