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Possibility of bound states obtained by perturbation theory

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It is well known that bound states cannot be obtained by Rayleigh-Schrödinger or Wigner-Brillouin perturbation theories. Here we apply a recently developed perturbation theory to the hydrogen atom, treating the full Coulomb potential as a perturbation. In first order we obtain a correction to the well-known Lifshitz method. The third order gives almost the exact result.

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I. INTRODUCTION

As far as we know, Wigner [1] was the first to try to calculate the bound states of the hydrogen atom by perturbation theory. He found the first order in the potential to vanish, the second order to give $E=-0.1093$ DRy, and all higher orders to diverge. The reason for this defect was shown by Macke, Ziesche, and Hausmann [2,3] to be a nonanalyticity of the series expansions of any quantity (such as E) at zero Coulomb coupling constant. Hausmann [3] succeeded in overcoming the divergencies of the perturbation theory, obtaining poles of the scattering matrix by solving approximately the homogeneous Born integral equation. His method, however, is restricted to one-dimensional problems with potentials of finite range.

Perturbation theory nowadays has experienced reviewed interest in solid-state physics in connection with the increasing importance of quantum wells, superlattices, etc. It is tempting to treat, e.g., the cation difference in a GaAs-Ga/AlAs superlattice as a small periodic perturbation over a homogeneous GaAs crystal and to understand band structures and phonon dispersion curves by folding those of the corresponding zinc-blende structure. This often is done in qualitative discussions. However, due to the importance of subbands, resulting from bound states of single quantum wells, any quantitative application of perturbation theory to superlattices makes sense only if bound states can be described at least approximately.

Another problem of interest related to the present work is the calculation of the density of states in impure semiconductors. With increasing concentration of, e.g., shallow donors, the hydrogenlike bound states are expected to broaden into, e.g., Lorentzian-shaped impurity bands, which then overlap with the conduction band. In order to interpret optical experiments, a theory is needed which is able to describe all bound states and results in extended band tails of the main and of the impurity bands. Band tails, however, cannot be obtained by the well-known coherent-potential approximation [4]. Besides, to our knowledge, this theory has never been applied to, and can hardly be used with, realistic donor potentials [5]. Klauder [6] proposed a simplified version of the coherent-potential approximation in which the so-called multiple-occupancy corrections are neglected, but which can be applied to realistic potentials. In this theory band tails are missing again [5].

The formation of extended band tails in impure semiconductors has been studied extensively by Lifshitz (see, e.g., [7]), but his method is based on an approximate solution of the impurity problem, which results in only one bound state. Hence, the problem of obtaining excited bound states in approximate theories is of interest for the description of impure semiconductors, and will be considered in this work, too.

Recently, one of us [8] developed a perturbation theory based on series expansions of the numerator as well as the denominator of the one-particle Green's function. This perturbation theory was originally introduced in order to obtain correct spectral weights in contrast to those of the Wigner-Brillouin perturbation theory, which is equivalent to a series expansion of a denominator—the self-energy, only. Subsequently, it was proved at the example of a δ-like potential [9] that this kind of perturbation theory yields bound states. In [9], however, the potential Fourier components $V(k=0)$ and $V(k\neq 0)\equiv V(k=0)$ have been treated in different ways.

Here we prove that the perturbation theory [8] gives the correct Koster-Slater [10] result for the δ-like potential if $V(k=0)$ and $V(k\neq 0)$ are treated uniformly. Then it is applied to the hydrogen atom with the full Coulomb potential as a perturbation. It is proved that the first order gives a correction to the Lifshitz approximation for bound states [7] and that already in third order almost the exact result is reproduced. The Coulomb potential being one of the worst possible cases, it can be concluded that this perturbation theory can also be successfully applied to, e.g., superlattice band-structure calculations.

II. GENERAL THEORY

The expansion coefficients a_n of the solution $\psi=\sum_n a_n\psi_n$ of the Schrödinger equation $H\psi=(H_0+V)\psi=E\psi$ into an orthonormal basis ψ_n of eigenstates of the unperturbed Hamiltonian $H_0\psi_n=\varepsilon_n\psi_n$ are given by

$$\sum_m [E-\varepsilon_n)\delta_{nm}-V_{nm}]a_m=0\ , \tag{1}$$

with $V_{nm}=(\psi_n, V\psi_m)$. This homogeneous linear system of equations has solutions only at the eigenvalues of $H\psi=E\psi$ which are determined by

$$\det[(E-\varepsilon_n)\delta_{nm}-V_{nm}]=0 \ . \tag{2}$$

Equation (2) is equivalent either to

$$\det(\delta_{nm}-W_{nm})=0 \tag{3}$$

with $W_{nm}=\dfrac{V_{nm}}{(E-\varepsilon_n)}$ or to

$$\det(\delta_{nm}-k_{nm})=0 \ , \tag{4}$$

where

$$k_{nm}=\frac{V_{nm}}{E-\varepsilon_n-V_{nn}}$$

has nondiagonal elements only, $k_{nn}=0$. Using the expansion theorem of determinants, we obtain from (3),

$$0=1-\sum_{q=1}^{\infty} W_{qq}+\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}d_n \ ,$$

with

$$d_n=\sum_{q_1,\ldots,q_n} d(q_1,\ldots,q_n)$$

$$=\sum_{q_1,\ldots,q_n=1}^{\infty}\begin{vmatrix} Wq_1q_1\ldots Wq_1q_n \\ Wq_2q_1\ldots Wq_2q_n \\ Wq_nq_1\ldots Wq_nq_n \end{vmatrix} \ . \tag{5}$$

From (4) we still obtain an alternative expansion

$$0=1+\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}e_n$$

with

$$e_n=\sum_{q_1\neq q_2\neq\cdots\neq q_n=1}^{\infty}\begin{vmatrix} 0 & kq_1q_2 & \cdots & kq_1q_n \\ kq_2q_1 & 0 & & kq_2q_n \\ \vdots & & & \\ kq_nq_1 & kq_nq_2 & & 0 \end{vmatrix} \ . \tag{6}$$

The solutions of (6) are identical with those derived in [8] from the perturbation theory for the one-particle Green's function. Up to the second order in V Eqs. (5) and (6), respectively, result in

$$1=\sum_n \frac{V_{nn}}{E-\varepsilon_n}-\frac{1}{2!}\sum_{n,m}\frac{V_{nn}V_{mm}-V_{nm}V_{mn}}{(E-\varepsilon_n)(E-\varepsilon_m)}+\cdots \tag{7}$$

and

$$1=\frac{1}{2!}\sum_{n\neq m}\frac{V_{nm}V_{mn}}{(E-\varepsilon_n-V_{nn})(E-\varepsilon_m-V_{mm})}+\cdots \ . \tag{8}$$

Equations (7) and (8) are symmetrized forms of the Wigner-Brillouin equations

$$E-\varepsilon_n-V_{nn}=\sum_{m\,(\neq n)}\frac{V_{nm}V_{mn}}{(E-\varepsilon_m)} \ . \tag{9}$$

The solutions for E of either (7), (8), or (9) contain, of course, higher orders in the potential V than the second one. It has still to be shown that the second-order expansions of these E coincide with the expressions of the conventional Rayleigh-Schrödinger perturbation theory. This is evident for the Wigner-Brillouin result (9), the deviations from

$$E=\varepsilon_n+V_{nn}+\sum_{m\,(\neq n)}\frac{V_{nm}V_{mn}}{(\varepsilon_n-\varepsilon_m)} \tag{10}$$

being of the third and of higher orders.

In the case of (8), we obtain for $E\approx\varepsilon_l$,

$$E-\varepsilon_l-V_{ll}=\frac{1}{2!}\sum_{n\neq m}\frac{(E-\varepsilon_l-V_{ll})V_{nm}V_{mn}}{(E-\varepsilon_n-V_{nn})(E-\varepsilon_m-V_{mm})}$$

$$=\sum_{n\,(\neq l)}\frac{V_{nl}V_{ln}}{(E-\varepsilon_n-V_{nn})}+\frac{1}{2!}\sum_{\substack{n\neq m\\(n,m\neq l)}}\frac{V_{nm}V_{mn}(E-\varepsilon_l-V_{ll})}{(E-\varepsilon_n-V_{nn})(E-\varepsilon_m-V_{mm})}$$

$$=\sum_{n\,(\neq l)}\frac{V_{nl}V_{ln}}{\varepsilon_l-\varepsilon_n}+\cdots \ .$$

The same is true in the case of (7).

In comparison with (10) Eqs. (9), (7), and (8) can be considered as special partial resummations of the perturbation series for E. Such a resummation, however, is necessary in the case of degenerate eigenvalues due to the divergency of the Rayleigh-Schrödinger series.

As shown in [8], the special Wigner-Brillouin resummation does not result in correct spectral weights in contrast to (7) and (8) as well as to the Rayleigh-Schrödinger result (10). Hence, in the case of degenerate eigenvalues, only the perturbation expressions (7) or (8) give reliable results.

The reason for this defect of the Wigner-Brillouin perturbation theory is the following: Suppose n is a discrete variable and is restricted by $n=1,\dots,N$. Then the eigenvalue equation (2) as well as, e.g., (8) give the correct number of N eigenvalues. The N nonlinear equations (9) yield a total number of $M>N$ eigenvalues, however, where M depend on the number of nonzero independent V_{nm}. If we have, e.g., a total number of N electrons within the system, the Wigner-Brillouin states can be occupied only by $N/M<1$ electrons in the mean, the density of states being given by

$$\rho(E)=\sum_n a_n\delta(E-E_n)\ \text{ with } a_n\neq 1\ ,$$

where the E_n are the solutions of (9). This was proved analytically in [8].

III. ONE-DIMENSIONAL EXAMPLE

In [9] it was shown that in the simplest case of a linear chain of N atoms with $\varepsilon_n=-\cos ka$, $k=2\pi n/N$, $n=0,\dots,N$ and $N\rightarrow\infty$ with a δ-like potential $V_{nm}\equiv V/N$ for all n and m, (8) results in bound and antibound states at $E=\pm\sqrt{1+\frac{1}{2}V^2}$ in contrast to the exact result

$$1=\frac{V}{N}\sum_n\frac{1}{E-\varepsilon_n}\xrightarrow[N\rightarrow\infty]{}E=\mathrm{sgn}(V)\sqrt{1+V^2} \tag{11}$$

of Koster and Slater [10].

The reason for this difference can be traced back to the different treatments of the diagonal $V_{nn}=V/N$ and the nondiagonal $V_{nm}=V/N$ matrix elements in (8): The diagonal elements are taken into account exactly, the nondiagonal ones being treated perturbationally despite the fact that all are identical. This shortcoming, however can be avoided, as follows.

With $V_{nn}\equiv V/N$ all d_n in (5) vanish, the eigenvalues being given by

$$0=1-V/N\sum_n\frac{1}{E-\varepsilon_n}\ .$$

In the same way we obtain in the one-dimensional case, with $\varepsilon=\hbar^2k^2/2m$ and $V(x)=-V\delta(x)$,

$$0\equiv 1+\frac{V}{2\pi}\int_{-\infty}^{+\infty}dk\frac{1}{E-\hbar^2k^2/2m}\ , \tag{12}$$

which can be integrated to give the exact result

$$E=-\frac{V^2m}{2\hbar^2} \tag{13}$$

for the bound state in an attractive δ potential in one dimension [3].

IV. HYDROGEN ATOM

Choosing as the orthonormal basis set the functions

$$\psi_{lmk}(r)=k\left[\frac{2}{\pi}\right]^{1/2}\psi_{lmj_l}(kr)\ ,$$

we obtain from (1),

$$\left[E-\frac{\hbar^2k^2}{2m}\right]a_{lmk}=\sum_{k'}a_{lmk'}V_l(k,k')\ , \tag{14}$$

with

$$V_l(k,k')=\frac{2kk'}{\pi}\int_0^{\infty}dr\,r^2j_l(kr)V(r)j_l(k'r) \tag{15}$$

in the case of a spherically symmetric potential $V(\mathbf{r})=V(r)$. s-like bound states then are obtained from

$$1=\int_0^{\infty}dk\frac{V(k,k)}{E-\hbar^2k^2/2m}-\frac{1}{2}\int_0^{\infty}dk\int_0^{\infty}dk'\frac{V(k,k)V(k',k')-V(k,k')V(k',k)}{\left[E-\frac{\hbar^2k^2}{2m}\right]\left[E-\frac{\hbar^2k'^2}{2m}\right]}+\cdots\ , \tag{16}$$

with

$$V(k,k')=\frac{2}{\pi}\int_0^{\infty}dr\sin(kr)V(r)\sin(k'r)\ . \tag{17}$$

In first order (16) and (17) can be written as

$$1=\int d^3k\frac{c(\mathbf{k})}{E-\frac{\hbar^2k^2}{2m}}\ , \tag{18}$$

with

$$c(\mathbf{k})=\frac{1}{(2\pi)^3}\int d^3r j_0^2(kr)V(r)\ . \tag{19}$$

Lifshitz (see, e.g., [7] and [11]) solved the eigenvalue problem of the Schrödinger equation approximately under the assumption that the potential vanishes with increasing r much more rapidly than the resulting wave function. This assumption becomes correct for δ potentials, which cannot be treated in three dimensions due to the divergency of

$$\int d^3k[1/(E-\hbar^2k^2/2m)]\ ,$$

however. The result of Lifshitz is an equation formally equivalent to (18), but with $c(\mathbf{k})$ being given by [11]:

$$c(\mathbf{k})=\frac{1}{(2\pi)^3}\int d^3rV(r)e^{-i\mathbf{k}\cdot\mathbf{r}}\ . \tag{20}$$

In the case of the Coulomb potential, (18) with (20) results in $E=-2$ DRy instead of $E=-0.5$ DRy.

We conclude that the approximate Lifshitz method is correct in first order in V if $c(\mathbf{k})$ is given for s states by (19) instead of (20). But (18), together with (19), cannot be applied to the Coulomb problem directly due to the divergency of the integral $\int_0^{\infty} dx(\sin^2 kx)/x$ in (19). This divergency reflects the fact that the kernel of the homogeneous Fredholm integral equation corresponding to (1) is singular in the Coulomb case (see, e.g., [12]). This difficulty can easily be circumvented by treating the problem within a finite three-dimensional spherical box of radius R and then taking the limit $R \to \infty$.

We restrict ourselves to s states and use atomic units $m=\hbar=e^2=1$. The complete set of s-like basis functions in a sphere of radius R with an infinite potential well is given by

$$\psi_n=\frac{\sin(n\pi r/R)}{\sqrt{2\pi R}\, r} ,$$

with $n=1,2,\ldots,\infty$. The potential matrix elements are then given by [1]

$$V_{nm}=-\frac{1}{R}\{\mathrm{ci}[(n-m)\pi]-\mathrm{ci}[(n+m)\pi]\} , \tag{21}$$

where ci(x) is the cosine integral

$$\mathrm{ci}(x)=\int_0^x \frac{\cos x'-1}{x'}dx' . \tag{22}$$

The unperturbed (kinetic) energy values are

$$\varepsilon_n=(\psi_n,H_0\psi_n)=\tfrac{1}{2}\left[\frac{n\pi}{R}\right]^2 . \tag{23}$$

Up to the fourth order, (5) results in

$$\begin{aligned}1=&\tfrac{1}{2}\sum_{n\neq m}^{M}\frac{V_{nm}V_{mn}}{E_nE_m}\\&+\tfrac{1}{3}\sum_{n\neq m\neq l}^{M}\frac{V_{nm}V_{ml}V_{\mathrm{ln}}}{E_nE_mE_l}\\&+\tfrac{1}{8}\sum_{n\neq m\neq l\neq k}^{M}\frac{2V_{nm}V_{ml}V_{lk}V_{kn}-V_{nm}V_{mn}V_{lk}V_{kl}}{E_nE_mE_lE_k}\end{aligned} \tag{24}$$

where

$$E_l=E-\tfrac{1}{2}\left[\frac{l\pi}{R}\right]^2-V_{ll} \tag{25}$$

and $M \to \infty$. (24) can be solved numerically for E, increasing M for a given R (measured in multiples of the Bohr radius) until convergency is obtained. This typically is fulfilled for $M \gtrsim 5R$.

Figure 1 gives the numerical results of the Wigner-Brillouin perturbation theory (9) together with those of Eq. (24) in the second and the third orders. In both cases the binding energies are measured relative to the first unperturbed kinetic energy $n=1$, according to Eq. (23), and not relative to $\frac{1}{2}(\pi/R)^2+V_{11}$, according to Eq. (25).

With increasing R, the binding energies in second and third order deviate from the exact result $E_0=-\frac{1}{2}$ DRy by only 22% and 12%, respectively. In the fourth order we obtained only a very slight improvement of the third-order result.

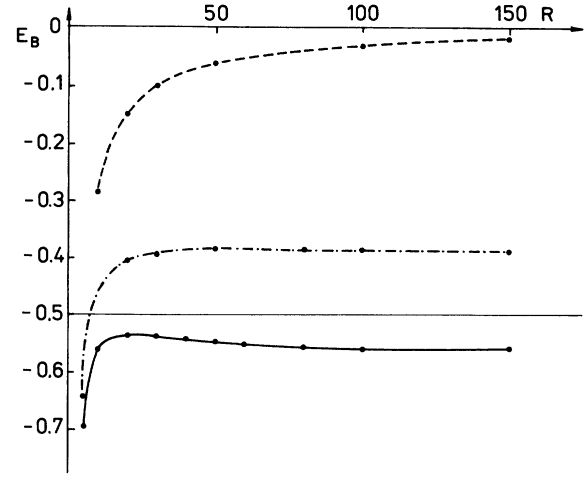

FIG. 1. Binding energy of the lowest bound states of the hydrogen atom in a finite sphere of radius R according to the second-order Wigner-Brillouin perturbation theory (· · ·) and according to the perturbation theory presented here in second (—·—·—·) and third (———) order. E_B is measured in DRy and R in Bohr radii.

The Wigner-Brillouin perturbation theory results in a vanishing with increasing R binding energy. The reason for this defect is the following: According to Eq. (21), V_{nm} vanishes with increasing R as

$$V_{nm}\sim\frac{1}{R} . \tag{26}$$

The asymptotic behavior for large R of the sum in Eq. (9) can be obtained from (26) together with the asymptotic integral representation of $\sum_{m=1}^{\infty}1/(E-\varepsilon_m)$. With $\Delta k=\pi/R$ and$k=m\Delta k$, we obtain for negative E,

$$\begin{aligned}\sum_{m=1}^{\infty}\frac{1}{E-\varepsilon_m}&=-\sum_{m=1}^{\infty}\frac{1}{|E|+\frac{1}{2}(m\pi/R)^2}\\&=-\frac{R}{\pi}\sum_{m=1}^{\infty}\frac{\Delta k}{|E|+\frac{1}{2}k^2}\\&\xrightarrow[R\to\infty]{}-\frac{R}{\pi}\int_0^{\infty}\frac{dk}{|E|+\frac{1}{2}k^2}\\&=-\frac{R}{\sqrt{2|E|}} .\end{aligned} \tag{27}$$

Therefore we get

$$\sum_{m=1}^{\infty}\frac{V_{nm}V_{mn}}{(E-\varepsilon_m)}\xrightarrow[R\to\infty]{}\frac{1}{R\sqrt{2|E|}} \tag{28}$$

and $\lim_{R\to\infty}E^{\mathrm{W.B.}}_{\mathrm{bound}}(R)=0$. Hence, the Wigner-Brillouin perturbation theory does not result in a bound state for $R \to \infty$.

The situation in the case of Eq. (24) is quite different: Each sum in the nth order has a nonvanishing limit for $R \to \infty$ with an energy dependence proportional to $(\sqrt{|E|})^{-n}$. Hence, independent of the order taken into account, the value $E=0$ cannot be a solution of Eq. (24).

The evaluation of Eq. (24) up to third order results in only one (s-like) bound state: For $E<\frac{1}{2}(\pi/R)^2+V_{11}$, all E_n are negative, hence, all terms in the second- and third-order sums increase monotonically from zero to $+\infty$ with increasing E from $-\infty$ up to $\frac{1}{2}(\pi/R)^2+V_{11}$. In the third order the binding energy of the second one moves to larger absolute values due to additional positive contributions on the right-hand side of Eq. (24). Only the occurrence of negative contributions in the right-hand side of Eq. (24) in fourth and higher orders can result in an oscillating-with-E behavior around the value 1 and, hence, in additional bound states.

Figure 2 shows the right-hand side of Eq. (7) up to the fourth order (for the case $R=20$ and $M=4$, convergency is not yet achieved). The oscillating behavior for negative E can clearly be seen.

We conclude that several (s-like in our case) bound states occur only due to sufficiently large negative contributions to the right-hand side of Eq. (24). This condition can be reformulated in the following way: (24) can be rewritten in the form of a decomposition into partial fractions:

$$1=\sum_n \frac{A_n}{E_n}\ ; \tag{29}$$

in (24) no multiple poles occur. Analogous to Eq. (27), the sum in (29) transforms into an integral for $R\rightarrow\infty$. With $E'=\frac{1}{2}k^2$, we obtain

$$1=\int_0^\infty \frac{A(E')dE'}{E-E'}\ , \tag{30}$$

where the right-hand side has the usual form of a spectral representation. As the A_n in (29), the function $A(E')$ contains contributions of all orders in the potential, among them negative contributions starting from the fourth order. If $A(E')$ has a fixed sign, the integral in (30) is a monotonic function of E and one obtains one bound state at best [in the case of a negative $A(E')$]. More than one bound state can occur only if $A(E')$ changes its sign at a certain E', which can never be the case up to third order. That is the reason why, e.g., the Lifshitz approximation (18) with (19) results in one bound state only for most potentials, including the Coulomb and the screened Coulomb one.

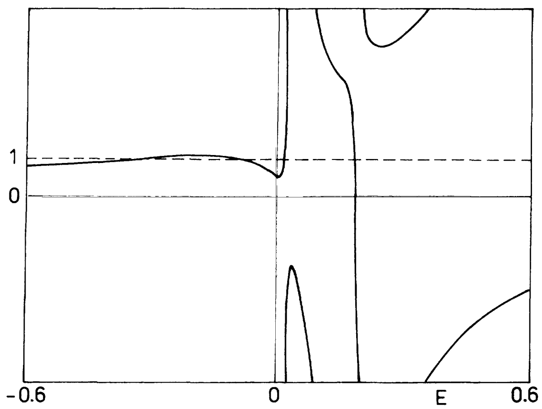

FIG. 2. Right-hand side of Eq. (8) up to the fourth order for the Coulomb potential in a three-dimensional spherical box of radius $R=20$ with $M=4$ (E in DRy).

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