Quasienergy spectra of a dipolar molecule and of the hydrogen atom

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The quasienergy operator has been constructed and its relation to the S-matrix has been established. Methods of approximate calculation of the quasienergy spectra are discussed. The quasienergy spectra of a dipolar molecule and of an excited hydrogen atom, i.e., systems with both permanent and induced dipole moments, have been found. A detailed discussion is given of the conditions for the appearance of the linear and quadratic Stark effects for such systems as functions of frequency and external field, and of the structure of the wave functions in the intermediate case.

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1. INTRODUCTION

The advent of quantum-mechanical generators producing coherent electromagnetic radiation has led to very considerable interest in the behavior of quantum-mechanical systems in high-intensity alternating electromagnetic fields. It has been necessary to develop a special formalism because the formalism of stationary quantum-mechanical states, i. e., states with definite energy, which, of course, occupies the central position in practically all the applications of quantum mechanics, is fundamentally unsuitable for an alternating field such as the field in an electromagnetic wave, because energy is not conserved in such a field. The most convenient and suitable for this particular physical situation is the formalism of quasienergy states, put forward virtually simultaneously by a number of authors (see the review in[1]), which makes use of the periodicity of the external field in time. The formalism of quasienergy states is a direct generalization of the formalism of stationary states but it enables us, among other things, to establish immediately the absorption, emission, and scattering spectra of a quantum-mechanical system in a strong alternating field. When the alternating field is adiabatically turned off, the quasienergy states become the usual stationary states.

The quasienergy states of free atoms, which are among the simplest quantum-mechanical objects, have been discussed and investigated by a substantial number of workers, both theoretically and experimentally.[2] However, the simplest atom, i. e., the hydrogen atom, has turned out to be the most difficult from the theoretical point of view. The reason for this is that the spectrum of the free hydrogen atom is degenerate in the orbital quantum number because, as is well known, even in a constant field, the hydrogen atom exhibits the linear Stark effect. This is its exclusive feature because all other atoms exhibit the quadratic effect under these conditions. At present, there are, therefore, two independent groups of papers, in one of which only the quadratic terms in the alternating electric field are taken into account,[3–5] while, in the other, only the linear terms are included.[6] As a result, the range of validity of either approximation is not well defined, and the existence of an intermediate region in which neither is satisfactory remains an open question.

The hydrogen-atom problem is a special case of a more general problem of the behavior of systems with both permanent and induced dipole moments in an alternating field. For example, published descriptions of dipolar molecules in alternating fields include either only linear[7] or only quadratic[8–10] quantities in the field.

The present paper is devoted to a consideration of these problems. In the next section, we shall construct the operator for which the eigenfunctions are the quasienergy states of the system. It may be referred to as the quasienergy operator. It will be shown that this operator differs by only a constant factor from the logarithm of the single-period S matrix describing the temporal evolution of the system in an external field. The spectrum of the quasienergy operator can readily be found when the field gives rise to strong mixing of only a finite number of stationary states of the system of which the quasienergy states are made up. The application of this formalism to the hydrogen atom is described in Sec. 4. Section 3 describes the mathematically simpler case of a dipolar molecule for which it is possible to formulate physically clearly the conditions for the validity of the various approximations. This leads to a better understanding of the situation in the general case.

2. QUASIENERGY OPERATOR

Consider the Schrödinger equation for a quantum-mechanical system in an external field that is a periodic function of time:

$$i\hbar\,\partial\psi/\partial t=H(t)\psi(t), \qquad H(t+T)=H(t). \tag{1}$$

The solution of this equation, which satisfies the condition

$$\psi_\varepsilon(t+T)=e^{-i\varepsilon T/\hbar}\psi_\varepsilon(t), \tag{2}$$

is called the quasienergy state corresponding to the quasienergy ε.

The quasienergy state is conveniently written in the form

$$\psi_\varepsilon(t)=e^{-i\varepsilon t/\hbar}\Phi_\varepsilon(t), \tag{3}$$

where Φ_ε is a periodic function of time. Expanding it into a Fourier series, we can obtain the quasienergy state in the form of a series in the quasienergy harmonics $\varphi_\varepsilon^{(n)}$

$$\psi_\varepsilon(t)=e^{-i\varepsilon t/\hbar}\sum_{n=-\infty}^{\infty}e^{-in\omega t}\varphi_\varepsilon^{(n)},\qquad \omega=2\pi/T. \tag{4}$$

It follows from the definition (2) that the modulus of the quasienergy is determined by $\hbar\omega$. Quasienergy states belonging to different values of quasienergy are mutually orthogonal. Different harmonics $\varphi_\varepsilon^{(n)}$ on the other hand, belonging to the same value of ε, are not, in general, orthogonal. Since the norm of the quasienergy states is independent of time, we have the following condition:

$$\sum_{n=-\infty}^{\infty}(\varphi_\varepsilon^{(n)},\varphi_\varepsilon^{(n+k)})=\delta_{k0},\quad k=\ldots-1,0,1,\ldots$$

We can use perturbation theory[3] to construct the quasienergy states and the quasienergy spectra for those cases for which the alternating field is small. The quasienergy states are also known for a free particle and a one-dimensional harmonic oscillator in an alternating field,[11] and for a particle in a constant magnetic field and in the field of an electromagnetic wave,[12] because (1) can be solved exactly for these systems. In the case of circularly polarized radiation Eq. (1) can also be solved for a particle bound by short-range forces because, after transformation to the rotating set of coordinates, the alternating field of the wave is found to be equivalent to a constant electric field crossed with a constant magnetic field.[13]

In many cases, nevertheless, it is desirable to have a sufficiently general algorithm for constructing quasienergy states and the quasienergy spectrum independently of perturbation theory and in a form which could be relatively simply used on modern computers. With this in view, let us introduce the evolution operator S defined by the equation

$$\psi(t)=S(t,t_0)\psi(t_0), \tag{5}$$

and satisfying the equation

$$i\hbar\frac{\partial}{\partial t}S(t,t_0)=H(t)S(t,t_0),\qquad S(t_0,t_0)=I, \tag{6}$$

where I is the unit operator. To be specific, let us suppose that $t_0=0$, and consider the single-period evolution operator $S(T,0)$.1) Since the operator satisfies the unitarity condition, it can be written in the form

$$S(T,0)=\exp\left\{-\frac{i}{\hbar}\tilde{H}T\right\}, \tag{7}$$

where $\tilde{H}$ is a time-independent self-adjoint operator which can be referred to as the quasienergy operator. In fact, substituting $t=0$ in (2), and comparing it with (5) and (7), we see that ε is the eigenvalue of $\tilde{H}$ and $\psi_\varepsilon(0)=\Phi_\varepsilon(0)$ is the corresponding eigenfunction. The quasienergy operator thus turns out to be (to within the factor $i\hbar/T$) the logarithm of the single-period S matrix

$$\tilde{H}=\frac{i\hbar}{T}\ln S(T,0). \tag{8}$$

For arbitrary t, the equation for $\Phi_\varepsilon(t)$ can readily be obtained from (1)–(7):

$$i\hbar\partial\Phi_\varepsilon/\partial t=[\mathbf{H}(t)-\tilde{H}]\Phi_\varepsilon(t),$$
$$\mathbf{H}(t)=\exp\left\{\frac{i}{\hbar}\tilde{H}t\right\}H\exp\left\{-\frac{i}{\hbar}\tilde{H}t\right\},$$
$$\tilde{H}\Phi_\varepsilon(0)=\varepsilon\Phi_\varepsilon(0),\quad \Phi_\varepsilon(T)=\Phi_\varepsilon(0).$$

In special cases, physical considerations can be used to isolate a finite number of levels which are highly mixed by the field. For example, the two-level approximation of the theory of interaction of resonance radiation with matter is well known. In such cases, the determination of the operator $S(t, 0)$ reduces to the construction of the fundamental matrix, i.e., the solution of a system of ordinary differential equations (6) in the interval $t\in[0, T]$. After diagonalization of this matrix at time $t=T$, the quasienergy spectrum is determined by the logarithms of the corresponding eigenvalues.

The formula given by (8) also enables us to apply well-known approximate methods to calculate the quasienergy spectra, since the matrix elements of $S(T, 0)$ can be interpreted as the amplitudes for transitions between given states. In particular, the variational principle of Schwinger, formulated for nonstationary systems in[14], and the various forms of the quasiclassical approximation,[11] may turn out to be useful.

Another method of obtaining the quasienergy spectrum, which is also effective for a limited number of states mixed by the field, is analogous to the well-known methods of finding the characteristic indices of ordinary differential equations with periodic coefficients, which belong to the Mathieu class of equations. Let $|\lambda\rangle$ represent the states of the unperturbed system mixed by the field. Expanding the quasienergy harmonics in (4) over this basis

$$\varphi_\varepsilon^{(n)}=\sum_\lambda a_\lambda^{(n)}|\lambda\rangle,$$

and substituting in (1), we obtain, after some fairly obvious transformations, the following set of linear homogeneous equations

$$\sum_{n\lambda'}[\langle\lambda|\mathscr{H}^{(m-n)}|\lambda'\rangle-(\varepsilon+m\hbar\omega)\delta_{mn}\delta_{\lambda\lambda'}]a_{\lambda'}^{(n)}=0, \tag{9}$$

where

$$\mathscr{H}^{(k)}=\frac{1}{T}\int_0^T dt\, e^{ik\omega t}H(t)$$

is the k-th Fourier harmonic of the Hamiltonian.

Summation over n in (9) is performed between $-\infty$ and $+\infty$, again for a finite number of states $|\lambda\rangle$. A natural approximation, therefore, is to determine the spectrum of the truncated matrix of coefficients in (9) with a restriction on the maximum value of $|n|$. The convergence of the approximations can be established by increasing the rank of this matrix.

Continuing our analogy with the Mathieu equation, we note that, in the case of this equation, the index λ assumes a unique value. For a chosen value of $|n|$, however, the diagonalization of the matrix will result, in this case, in $2|n|+1$ eigenvalues. As $|n|$ increases, the difference between these numbers should tend to integral multiples of $\hbar\omega$ because they are all values of the same quasienergy. Success in the choice of the given value of $|n|$ can therefore be used as a check in this respect as well.

To remove the discrete ambiguity in the quasienergy, the usual procedure is to choose its value so that the adiabatic introduction of the variable-field amplitude ensures that the quasienergy becomes equal to the eigenvalue of the stationary Hamiltonian corresponding to the wave function which then becomes the limit to which the quasienergy state tends. This approach is adopted in the present paper.

3. DIPOLAR MOLECULE

Consider a linearly polarized field which is used as a perturbation on the states $|Jm\rangle$ of a molecule, where J is the total angular momentum and m is its component in the direction of the electric field of the wave. The other quantum numbers are not explicitly shown for the sake of brevity. The quantum number m is conserved even after the field is turned on because, in the case of linear polarization, the Hamiltonian for the molecule remains axially symmetric. In precisely the same way, axial symmetry is conserved in the case of circularly polarized waves except that the corresponding direction turns out to be parallel to the direction of propagation of radiation, which is the spectroscopic stability principle of Bohr and Heisenberg. The two cases are, therefore, analogous apart from the difference just mentioned.

The situation is much more complicated in the case of elliptically polarized fields in which the magnetic quantum number is not conserved and the mixing of states with different m by the field must be taken into account. This case will not be considered here because our present aim is to elucidate the relative role of permanent and induced dipole moments, and in this problem the polarization of the field is not of fundamental importance. The behavior of a molecule with only the induced dipole moment in an elliptically polarized field is described in[10].

We shall also assume that the energy of the interaction between the molecule and the field is much less than the energy interval between the rotational levels. Under these conditions, the total angular momentum of the molecule will continue to be conserved despite the violation of the spherical symmetry of the original Hamiltonian because the effect of the field is not sufficient to mix states with different rotational quantum numbers. The mixing of rotational levels by the field in the presence of only the induced dipole moment is discussed in[10]. A similar problem for a molecule with a permanent dipole moment is discussed in[10]. The problem of a molecule with a permanent dipole moment in a constant electric field has been discussed by a number of workers (the references can be found in in[7,10]). In both cases, as the field is increased, the spectrum is transformed from rotational to oscillator type.

Subject to the above restrictions, the solution of the Schrödinger equation for the molecule can be sought in the form

$$\psi_{Jm}(t)=\sum_j a_j(t)\,e^{-iE_jt}|jm\rangle, \tag{10}$$

where j are the quantum numbers of virtual states and $\hbar=1$.

The interaction of the molecule with the field in the dipole approximation takes the form

$$V(t)=-d_zF\cos\omega t, \tag{11}$$

where $\mathbf{d}$ is the dipole-moment operator and F is the amplitude of the electric field of the wave, which can be a slowly varying function of time. In particular, $F(t\to-\infty)=0$.

In second-order perturbation theory in the interaction given by (11), the required coefficient a_J is given by

$$\begin{gathered}i\dot a_J(t)=\langle Jm|V(t)|Jm\rangle a_J(t)-i\sum_{j\neq J}\langle Jm|V(t)|jm\rangle\\ \times\int_{-\infty}^{t}\langle jm|V(t')|Jm\rangle\exp\{i\omega_{Jj}(t-t')\}\,a_J(t')\,dt',\\ \omega_{Jj}=E_J-E_j.\end{gathered} \tag{12}$$

Usually, the equation given by (12) is replaced by an equation in which, on the right-hand side, the zero-order iteration has already been performed: $a_J=1$. In the present case, the quantity a_J is not assumed constant, but we will assume that it varies much more slowly than the function under the integral in (12). In view of this assumption (its validity will be considered later), the coefficient a_J can be taken outside the integral sign and the result is

$$\begin{gathered}i\dot a_J=\Big[-d_0F\cos\omega t+\frac{F^2}{4}\sum_{j\neq J}|\langle Jm|d_z|jm\rangle|^2\\ \times\Big(\frac{1+e^{2i\omega t}}{\omega_{Jj}-\omega}+\frac{1+e^{-2i\omega t}}{\omega_{Jj}+\omega}\Big)\Big]a_J,\end{gathered} \tag{13}$$

where $d_0=\langle Jm|d_z|Jm\rangle$ is the mean value of the component of the constant dipole moment of the molecule in the particular state along the direction of the electric vector of the wave.

Consider, to begin with, low frequencies

$$\omega\ll|\omega_{Jj}|\quad\text{for all}\quad j\neq J. \tag{14}$$

In practice, this means that the field frequency is small in comparison with the rotational constant. If this is so, we can neglect ω in the denominators in the sum in (13), which means that the dynamic polarizability of the molecule at low frequencies is replaced by the static value α. The result of all this is that

$$\begin{gathered}i\dot a_J=\Big(-d_0F\cos\omega t-\frac{\alpha F^2}{2}\cos^2\omega t\Big)a_J,\\ a_J(t)=\exp\Big\{i\frac{d_0F}{\omega}\sin\omega t+i\frac{\alpha F^2}{4}\Big(t+\frac{\sin 2\omega t}{2\omega}\Big)\Big\}.\end{gathered} \tag{15}$$

It is clear from (15) that the quasienergy of the molecule in the field is determined by the polarizability, i. e., $\varepsilon = -\alpha F^2/4$. The permanent dipole moment affects only the quasienergy harmonics:

$$a_J(t)=\exp\left\{i\frac{\alpha F^2}{4}t\right\}\sum_{n=-\infty}^{\infty}a_J^{(n)}e^{-in\omega t},$$

$$a^{(n)}=\frac{1}{2\pi}\int_0^{2\pi}\exp\left\{i\frac{d_0F}{\omega}\sin\theta+i\frac{\alpha F^2}{8\omega}\sin 2\theta+in\theta\right\}d\theta. \tag{16}$$

Expressions of the form given by (16) have been investigated by Nikishov and Ritus in[15] in connection with multiphoton processes in the case of a free relativistic particle in the field of a plane electromagnetic wave. Expansions in terms of the Bessel functions can also be readily obtained:

$$a_J^{(n)}=\sum_{s=-\infty}^{\infty}(-1)^n J_{n+2s}\left(\frac{d_0F}{\omega}\right)J_s\left(\frac{\alpha F^2}{8\omega}\right). \tag{17}$$

When the quadratic terms are small, i. e.,

$$\alpha F^2/8\omega\ll 1, \tag{18a}$$

the main term in (17) is that corresponding to $s=0$, and the harmonic $a_J^{(n)}$ is determined by a single Bessel function. These expressions for $a_J^{(n)}$ were used in[7].

If, in addition to (18a), we have the condition

$$d_0F/\omega\ll 1, \tag{18b}$$

the zero-order harmonic $a_J^{(0)}$ is the largest, and the shift in the energy of the molecule is determined only by its quasienergy, i. e., it is quadratic in the field. A linear shift may, therefore, appear only under a condition opposite to that given by (18b), i. e.,

$$d_0F/\omega\gg 1. \tag{19}$$

In this case, the expression given by (16) can be estimated by the saddle point method. The saddle points are determined, as usual, from the condition that the argument of the exponential in (16) is an extremum:

$$\cos\theta_{1,2}=-\frac{a}{8b}\pm\left[\frac{a^2}{64b^2}-\frac{n}{4b}+\frac{1}{2}\right]^{1/2},\quad a=\frac{d_0F}{\omega},\quad b=\frac{\alpha F^2}{8\omega}.$$

The largest of the harmonics $a_J^{(n)}$ is that for which the second derivative of the argument of the exponential at the point $\theta_{1,2}$ has the minimum absolute value. Using this, we find that the number of the maximum harmonic is

$$n_0=2b-a=\alpha F^2/4\omega-d_0F/\omega.$$

For this value of n_0, the absolute value of the argument of the exponential is also small, in contrast to the second value n, which is not cited here for this reason. Substituting n_0 in (16), we see that, because of the existence of the region of maximum harmonics with $n\approx n_0$, measurement of the energy of the molecule by means of radiation, absorption, or scattering processes will yield the same value, as if the energy of the molecule has undergone a linear shift d_0F in the field.

It is clear, however, that the linear shift will be recorded only when the number of large harmonics is small, i. e., the distribution of the numbers of these harmonics is sufficiently narrow. The width Δn of the distribution in the region of n_0 can be found by considering the third derivative of the argument of the exponential in (16). The inequality $\Delta n/n_0\ll 1$ is satisfied provided

$$d_0F\gg\alpha F^2/4, \tag{20}$$

and the physical significance of this is quite clear.

Thus, the linear level shift in the field occurs when the inequalities given by (19) and (20) are simultaneously satisfied. When (19) is not satisfied, the shift is quadratic in the field. When (19) is satisfied but (20) is not, the situation is more complicated because both linear and quadratic terms are important. When this is so, the wave function contains a large number of quasienergy harmonics (17) with comparable weights.

Let us now consider the validity of the assumptions made above.

Firstly, the restriction to the region of low frequencies, defined by (14), is not essential because, at high frequencies, comparable with the rotational constant, the condition given by (19) can be satisfied only in fields in which the total angular momentum of the molecule is no longer conserved. Hence, for such frequencies, there is either a quadratic level shift or, in strong fields, a radical rearrangement of the molecular spectrum.

Secondly, the condition that the frequency of the coefficient a_J be small is necessary to ensure that the transition from (12) to (13) takes place in accordance with the expressions obtained for a_J provided

$$d_0F,\ {}^1\!/_4\alpha F^2\ll|\omega_{Jj}\pm\omega|, \tag{21}$$

which means that the energy of interaction between the molecule and the field is small in comparison with the resonance detuning between the field frequency and the characteristic frequency of the molecule. When (21) is not satisfied, there is an essential rearrangement of the molecular spectrum in the resonance-frequency field.

4. HYDROGEN ATOM 2)

When we consider the states of the hydrogen atom corresponding to the shell with principal quantum number n, we shall assume that the interaction between the atom and the incident radiation is much greater than the spin-orbital splitting, so that the latter can be entirely neglected. On the other hand, the interaction with the radiation is much less than the separation from the neighboring higher shell with principal quantum number $n+1$, so that the admixture of all the other states to the particular state in shell n can be taken into account through perturbation theory.

Suppose that the electric vector of a linearly polarized wave lies along the z axis. In this case, the component of the orbital angular momentum along the z axis is conserved, and the wave function for the hydrogen atom in the field can be sought in the form (we shall be using the atomic system of units)

$$\psi_{nm}(t)=\sum_{l} A_l e^{-iE_n t}|nlm\rangle+\sum_{NL\neq nl} B_{NL} e^{-iE_N t}|NLm\rangle. \tag{22}$$

The coefficients A and B satisfy the following set of equations:

$$\begin{aligned} i\dot{A}_l &= \sum_{l'} \langle nlm|V(t)|nl'm\rangle A_{l'}(t) \\ &+\sum_{NL} \langle nlm|V(t)|NLm\rangle e^{i\omega_{nN}t} B_{NL}(t), \\ i\dot{B}_{NL} &= \sum_{l} \langle NLm|V(t)|nlm\rangle \exp\{i\omega_{Nn}t\} A_l(t) \\ &+\sum_{N'L'} \langle NLm|V(t)|N'L'm\rangle \exp\{i\omega_{NN'}t\} B_{N'L'}(t). \end{aligned} \tag{23}$$

To take into account the admixture of coefficients B in coefficients A in accordance with perturbation theory, we shall omit the second term on the right-hand side of the second equation in (23) and will integrate the resulting equation with respect to time. The result of this is then substituted in the first equation in (23):

$$\begin{aligned} i\dot{A}_l &= \sum_{l'} \langle nlm|V(t)|nl'm\rangle A_{l'}(t) \\ &-i\sum_{l',NL} \langle nlm|V(t)|NLm\rangle \int_{-\infty}^{t} \langle NLm|V(t')|nl'm\rangle \exp\{i\omega_{nN}(t-t')\} A_{l'}(t')\,dt'. \end{aligned} \tag{24}$$

Since the restriction on the field $V \ll \omega_{n+1,n}$ has already been imposed in the derivation of (24), analysis of these equations must be carried out only in relation to the values of the two parameters $\omega/\omega_{n+1,n}$ and V/ω. When $\omega \sim \omega_{n+1,n}$, the first term on the right-hand side of (24) oscillates rapidly in comparison with the fundamental harmonic of the coefficients A, whose time dependence is determined by the quasienergy ε since it is clear that the quasienergy must be proportional to a power of the small parameter V (the second power in the case of the lowest-order perturbation theory). The slowly-varying contributions of the first positive and negative harmonics of A can readily be shown to cancel one another out. When the quasienergy operator is constructed, therefore, the terms that are linear in V can be ignored and so can the rapidly oscillating components in the term that is quadratic in V. The resulting equations describe the quadratic Stark effect in a high-frequency field and were discussed previously in[3–5]. Most of the interest, therefore, attaches to the case of low frequencies $\omega \ll \omega_{n+1,n}$ [compare this with (14)], and we shall confine our attention to this case.

In this limit, the time factor $\exp\{i\omega_{Nn}t'\}$ under the integral sign in (24) varies much more rapidly than V and A, whose variation frequency is of the order of ω, ε. These quantities can therefore be taken outside the integral sign. Numerical analysis based on the results reported in[5] for the $n=2$ shell with $\omega \approx 0.1$ eV shows that precise allowance for the time dependence of the interaction V modifies the result by no more than a few percent. A comparable contribution is clearly provided by the time dependence of the unknown coefficient A if the weights of the harmonics with numbers $k \approx \omega_{n+1,n}/\omega \gg 1$ in this coefficient are negligible and this occurs for $V \ll \omega_{n+1,n}$. We note that, as in the case of the dipolar molecule, this approximation corresponds to the replacement (at low frequencies) of the dynamic polarizability by its static value.

F	ε_1	ε_2	$\bar{\varepsilon}$	F	ε_1	ε_2	$\bar{\varepsilon}$
1	0.034	0.050	0.042	6	1.50	1.52	1.51
2	0.161	0.175	0.168	7	2.08	2.03	2.06
3	0.392	0.364	0.378	8	2.69	2.68	2.69
4	0.680	0.663	0.672	9	3.37	3.43	3.40
5	1.031	1.069	1.050	10	4.20	4.20	4.20

Note. All the quantities are given in units of 10^{-3} a.u.

The final expressions have the form

$$\begin{aligned} i\dot{A}_l &= -F\cos\omega t \sum_{l'} \langle nlm|d_z|nl'm\rangle A_{l'} \\ &+F^2\cos^2\omega t \sum_{l',NL\neq nl} \frac{1}{\omega_{nN}} \langle nlm|d_z|NLm\rangle \langle NLm|d_z|nl'm\rangle A_{l'}. \end{aligned} \tag{25}$$

Solutions of (25) with only one term linear in F were analyzed in[6]. A solution without the linear term and with the substitution

$$\cos^2\omega t \to {}^1/_2, \quad 1/\omega_{nN} \to \omega_{nN}/(\omega_{nN}^2-\omega^2)$$

was considered, as already noted, in[3–5]. In general, Eq. (25) cannot be integrated analytically. In the simple case of $n=2$, to which we shall confine our attention here, the matrix form of (25) is

$$i\dot{\mathbf{A}}=\begin{pmatrix} {}^1/_2\,\alpha_1 F^2\cos^2\omega t & \beta F\cos\omega t \\ \beta F\cos\omega t & -{}^1/_2\,\alpha_2 F^2\cos^2\omega t \end{pmatrix}\mathbf{A}, \quad \mathbf{A}=\begin{pmatrix} A_s \\ A_p \end{pmatrix}. \tag{26}$$

Numerical values of the matrix elements were determined by the method described in[5], and it was found that $\alpha_1=120$, $\alpha_2=216$, $\beta=3$.

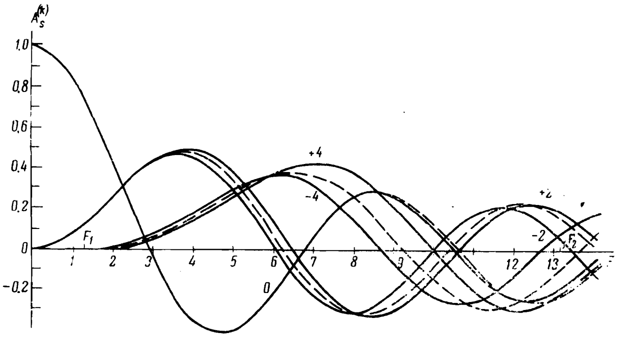
Equation (26) can be looked upon as a Schrödinger equation in a finite-dimensional space, which arises as a result of the foregoing simplifiying assumptions. To find the corresponding quasienergy spectrum, we use the device described in Sec. 2. We first solve Eq. (6), in which the Hamiltonian is determined by the matrix in (26) by means of iteration. To determine the quasienergies to within F^4, we must perform three iterations, and the result of this is

$$\begin{aligned} \varepsilon_1 &= -\frac{1}{4}\alpha_1 F^2+\frac{\beta^2F^4}{16\omega^2}\left(\frac{3}{2}\alpha_1-\alpha_2\right), \\ \varepsilon_2 &= -\frac{1}{4}\alpha_2 F^2+\frac{\beta^2F^4}{16\omega^2}\left(\frac{3}{2}\alpha_2-\alpha_1\right). \end{aligned} \tag{27}$$

Quantities $\sim F^2$ determine the energy shifts of the atomic levels due to the ordinary polarizability. The expressions given by (27) can also be used to derive the following condition under which the permanent dipole moment, which is determined by β, can be neglected in an alternating field:

$$(\beta F)^2 \ll \omega^2. \tag{28}$$

The above table lists values of quasienergies corresponding to the above states of the hydrogen atom, found by numerical solution of (6) with the Hamiltonian given by (26) and $\omega=0.1$ eV ≈ 0.0037 a.u. (the frequency range of the CO_2 laser). In the limit of a very weak field, the value of ε_1 is determined by the polarizability of the $2s$ state, which is equal to α_1, and ε_2 is



Weights of quasienergy harmonics for the 2s state as functions of the wave field (in multiples of 10^{-3}a.u.). Numbers of harmonics are shown against the curves.

determined by the polarizability of the 2p state, which is equal to α_2. Condition (28) is violated in this frequency when $F \approx 10^{-3}$ a.u. $= 5 \times 10^6$ V/cm.

It is clear from the table that the quasienergies ε_1 and ε_2 approach one another as F increases. This behavior is explained by the presence of the small numerical parameter in (26). To determine this parameter, it is useful to substitute

$$A_s + A_p = 2B_1, \quad A_s - A_p = 2B_2,$$

$$i\dot{\mathbf{B}} = \begin{pmatrix} \beta F \cos\omega t - \frac{\alpha_1+\alpha_2}{4} F^2\cos^2\omega t & \frac{\alpha_2-\alpha_1}{4} F^2\cos^2\omega t \\ \frac{\alpha_2-\alpha_1}{4} F^2\cos^2\omega t & -\beta F\cos\omega t - \frac{\alpha_1+\alpha_2}{4} F^2\cos^2\omega t \end{pmatrix}\mathbf{B}. \tag{29}$$

The values of the parameters $\alpha_{1,2}$ indicate that the nondiagonal matrix elements in (29) are smaller than the diagonal elements in the ratio of $(\alpha_2 - \alpha_1)/(\alpha_2 + \alpha_1) \approx \frac{1}{4}$. Rejecting the nondiagonal terms, we obtain the following approximate solution:

$$A_{s,p} = \exp\left\{ i\frac{\bar{\alpha}}{4}F^2 t + i\frac{\bar{\alpha}F^2}{8\omega}\sin 2\omega t \right\} \times\left[C_1 \exp\left\{ -i\frac{\beta}{\omega}F\sin\omega t \right\} \pm C_2 \exp\left\{ i\frac{\beta}{\omega}F\sin\omega t \right\} \right], \tag{30}$$

where $\bar{\alpha} = (\alpha_1 + \alpha_2)/2$. The upper sign corresponds to s, and the lower to p. $C_{1,2}$ are arbitrary constants, for example, if the atom were in the 2s state prior to the introduction of the field, then $C_1 = C_2 = \frac{1}{2}$.

The functions given by (30) correspond to the degenerate quasienergy spectrum $\bar{\varepsilon} = \bar{\alpha}F^2/4$ in the third column of the table.

Since the functions given by (30) turn out to be identical with (16), we can use the analysis of these quantities given in the preceding section. In particular, the energy levels of the hydrogen atom undergo a linear shift and a splitting when

$$\beta F \gg \omega, \quad \beta F \gg \bar{\alpha}F^2/4.$$

For the frequency which we are considering, these two inequalities are satisfied in the region of $F \approx 5 \times 10^7$ V/cm.

The solid curves in the figure show the behavior of the first even harmonics of A_s for initial conditions $C_{1,2} = \frac{1}{2}$. The broken curve represents the same harmonics when the quadratic terms $\sim \bar{\alpha}F^2/4$ are neglected. When $F \ll F_1 = \omega/\beta$, all the quasienergy harmonics are negligible in comparison with the zeroth harmonic. The second characteristic value of the field beyond which the quadratic terms contribute to the weights of the harmonics [see (18a)] is $F_2 = (8\omega/\bar{\alpha})^{1/2} \approx 10F_1$ at the above frequency. In this case, therefore, the region in which the quasienergy harmonics with appreciable weight are described by one term from (17) is practically absent. Nevertheless, it is clear from the figure that the linear terms reproduce the behavior of the zeroth harmonic quite well, but the importance of the quadratic terms increases rapidly as $|k|$ increases. The quadratic terms also lead to a difference between the weights of harmonics with different signs of of their number, whereas, when these terms are ignored, the weight of a harmonic is determined only by the absolute value of the number.

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[1)] In the mathematical literature, this operator is referred to as the monodromy operator.

[2)] The main results presented in this section were communicated to the All-Union Seminar on Multiphoton Spectroscopy which was held in Chernogolovka in 1974.

[1] Ya. B. Zel'dovich, Usp. Fiz. Nauk **110**, 139 (1973) [Sov. Phys. Usp. **16**, 427 (1973)].
[2] N. B. Delone, V. P. Kraĭnov, and V. A. Khodovoĭ, Usp. Fiz. Nauk **117**, 189 (1975) [Sov. Phys. Usp. **18**, 750].
[3] V. I. Ritus, Zh. Eksp. Teor. Fiz. **51**, 1544 (1966) [Sov. Phys. JETP **24**, 1041 (1967)].
[4] Y. Gontier and M. Trahin, Phys. Rev. A **7**, 191 (1973).
[5] B. A. Zon, N. L. Manakov, and L. P. Rapoport, Opt. Spektrosk. **38**, 13 (1975) [Opt. Spectrosc. (USSR) **38**, 6 (1975)].
[6] V. A. Kovarskii and N. F. Perel'man, Zh. Eksp. Teor. Fix. **60**, 509 (1971) [Sov. Phys. JETP **33**, 274 (1971)].
[7] C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw, 1955.
[8] V. P. Yakovlev, Zh. Eksp. Teor. Fiz. **53**, 987 (1967) [Sov. Phys. JETP **26**, 592 (1968)].
[9] P. A. Braun and A. N. Petelin, Zh. Eksp. Teor. Fiz. **66**, 1581 (1974) [Sov. Phys. JETP **39**, 775 (1974)].
[10] B. A. Zon and B. G. Katsnel'son, Zh. Eksp. Teor. Fiz. **69**, 1166 (1975) [Sov. Phys. JETP **42**, 595 (1975)].
[11] A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, Rasseyanie, reaktsii i raspady v nerelyativistskoĭ kvantovoĭ mekhanike (Scattering Reactions and Decays in Nonrelativistic Quantum Mechanics), Nauka, 1971.
[12] R. Redmond, J. Math. Phys. **6**, 1163 (1965).
[13] N. L. Manakov and L. P. Rapoport, Zh. Eksp. Teor. Fiz. **69**, 842 (1975) [Sov. Phys. JETP **42**, 430].
[14] S. Altshuler and J. E. Carlson, Phys. Rev. **95**, 546 (1954).
[15] A. I. Nikishov and V. I. Ritus, Zh. Eksp. Teor. Fiz. **46**, 776 (1964) [Sov. Phys. JETP **19**, 529 (1964)].

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