The range of the parameters is $\mu_i \geqslant 0$, with $\sum \mu_i = 1$, and $-1 \leqslant v \leqslant 1$.

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APPENDIX

An alternative parametrization of a positive definite Hermitian matrix ρ is

$$\rho = \exp H, \tag{17}$$

where H is any Hermitian matrix. For let H be diagonalized by a unitary transformation, so that its diagonal elements h_i are real numbers. Then ρ, as defined by Eq. (17) will also be diagonal, with diagonal elements $\lambda_i = \exp(h_i)$ which are real positive numbers. Conversely, let ρ be a positive definite Hermitian matrix, diagonalized by the unitary matrix U, and with real positive eigenvalues λ_i. Let H_d be a diagonal matrix, with diagonal elements $h_i = \ln\lambda_i$, which are real numbers. Then $H \equiv U H_d U^\dagger$ is Hermitian and ρ is given by Eq. (17). We observe that there is one and only one logarithm of a positive definite Hermitian matrix, which is Hermitian. This parametrization is perhaps less convenient than the one discussed in the text. In fact any mapping f of the whole real line allows the parametrization $\rho = f(H)$.

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Scattering Resonances and Metastable States in Wave Equations

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In the neighborhood of scattering resonances, the plane-wave solutions are strongly altered and low-order perturbation theory breaks down. Instead of calculating and using the exact scattering solutions there are many advantages to introducing the quasistationary concept of metastable localized eigenfunctions, by means of which the nonperturbative behavior near resonances can be described, whereas nonlocalized features are given by plane-wave functions. It is shown how metastable eigenfunctions can be defined in a natural way without arbitrariness. It is found that a number of general relations have to be satisfied by the metastable functions, which helps to approximate them in the case of a special problem.

I. INTRODUCTION

IN an unrestricted and uniform, but not necessarily isotropic, space or lattice, all wave equations (classical, quantum-mechanical, continuous, or discrete) have plane-wave eigensolutions. They are basic functions of irreducible representations to the respective space group and can only be normalized to the δ function.

If there is a localized region of disturbance, there is always some difficulty in handling both localized and nonlocalized features simultaneously. The wave functions for discrete energy levels are necessarily localized. For continuous (or quasicontinuous) energy sequences, on the other hand, the plane-wave solutions may be used for a low-order perturbation theory. Such a procedure breaks down, however, if there are scattering resonances, i.e., if the wave amplitude in the disturbed region exceeds strongly the amplitude outside. One has the phenomenum of a quasilocalized state. Yet, belonging to a continuous set of eigenvalues, it is impossible to normalize an exact eigenfunction to a finite value.

It is therefore advisable to abandon the rigid concept of stationary solutions in favor of a metastable solution which can be normalized and has, because of its slow decay, almost the features of a stationary state. Provided that it is possible to define (i.e., to localize) in a natural way the metastable function $\phi(0)$ belonging to some given scattering resonance, and also that we know the dissipation $\phi(t)$ of this localized state in time, such a concept has two essential advantages:

(a) Let $\psi(0)$ be an arbitrary wave packet at $t=0$, $\langle\psi(0)|\phi(0)\rangle$ its projection onto the normalized metastable state. Then one can show that the difference $\Delta\psi(0) = \psi(0) - \langle\psi(0)|(0)\rangle\phi(0)$ proceeds in time very nearly as if there were no scattering at all,

$$\Delta\psi(t) = \int a(\mathbf{k})\phi_{\mathbf{k}}{}^{(0)} e^{-i\omega(\mathbf{k})t} d^3k, \tag{1}$$

$$a(\mathbf{k}) = \langle\Delta\psi(0)|\phi_{\mathbf{k}}{}^{(0)}\rangle, \tag{1a}$$

where $\phi_{\mathbf{k}}{}^{(0)}(\mathbf{r})$ are the eigensolutions of the uniform space. We may, therefore, write the time behavior of the whole packet $\psi(0)$ as

$$\psi(t) = \langle\psi(0)|\phi(0)\rangle\phi(t) + \int a(\mathbf{k})\phi_{\mathbf{k}}{}^{(0)} e^{-i\omega(\mathbf{k})t} d^3k. \tag{2}$$

If there is more than one resonance, we have naturally to consider the projections to the other metastable

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states also. We remember now that the physical properties of a system (described by a wave equation) are known, if we know the time behavior of any arbitrary wave packet given at $t=0$. Hence, the dynamical behavior of a system with a localized disturbance is approximately given by its metastable functions and the free space solutions, and a low-order perturbation theory is applicable for further improvement.

(b) For the investigation of transport processes (electric conduction, heat conduction) the concept of metastable states is even preferable to the exact stationary solution. Namely, in the neighborhood of scattering resonances it is impossible to define a spatially constant group velocity for moving particles or phonons, as the particles are delayed in the scattering region. Hence, it is impossible to establish a Boltzmann equation[1] in the usual way. Instead one has to introduce more complicated methods. This, however, is not necessary if one adopts the concept of a metastable state. For now one may use the group velocities of the uniform space for the moving particles; but one has the new possibility that the particles are captured in a metastable state, where they no longer contribute to the current at all, and are re-emitted. This concept has been introduced by Wagner[2] in a phenomenological way to calculate the thermal conductivity of a crystal with impurity centers.

What, then, is the most fundamental property of a metastable state? Since a true eigenfunction of a discrete energy E_n is characterized by a time-independent functional form, apart from a time-periodic amplitude factor, we postulate that the functional form of a metastable state be also time-independent, whereas the amplitude decreases exponentially,[3]

$$\phi(t)=\phi(0)\exp[-[(iEt/\hbar)-(\Gamma t/2\hbar)]]. \tag{I}$$

This postulate is in agreement with a recent study of Newton,[4] in which it is *proved* that there is a delayed emergence of particles associated with any sufficiently sharp resonance that under suitable conditions follows an experimental law of decay over many lifetimes (of the "metastable state"). It is clear that such a behavior is only possible in a restricted, finite region, because otherwise it would contradict the conservation of probability. Consequently, the metastable function must be zero outside of a characteristic volume v,

$$\phi(0)\equiv 0 \text{ outside } v. \tag{II}$$

We consider this as a second fundamental property of a metastable function, although, strictly speaking, it is a consequence of (I).

From this we see that an investigation of metastable states has two essential tasks: (1) the evaluation of the functional form ϕ and (2) the definition of the localization volume v. It is the purpose of this paper to derive ϕ from the scattering solutions near the resonance and to show that the localization area can be defined without arbitrariness. It is this feature which distinguishes our study from the work of Wigner and Eisenbud[5] and from that of Kapur and Peierls[6]; in these investigations the arbitrary choice of a fixed boundary surface for the internal region is inevitable, whereas in the present work the boundary follows in a natural way from the formalism. The exact definition of a metastable function (Sec. VII) even does not incorporate any choice of the boundary. In addition we shall find a number of very interesting properties by means of which one can select suitable methods of approximations for ϕ as well as for the scattering solutions in the resonance region.[7,8]

II. GREEN'S FUNCTION FORMALISM

For our investigation we choose the quantum-mechanical wave equation of an electron, to avoid any confusion. The results are easily modified for other wave equations and unchanged in principle. Let H_0 be the free space Hamiltonian and V the localized scattering potential,

$$H=H_0+V. \tag{3}$$

Then the plane-wave solutions of H_0 are given by

$$\phi_{\mathbf{k}}(\mathbf{r})=(2\pi)^{3/2}e^{i\mathbf{k}\cdot\mathbf{r}},\quad E(\mathbf{k})=(2m/\hbar^2)k^2,\qquad \langle\phi_{\mathbf{k}}|\phi_{\mathbf{k}'}\rangle=\delta(\mathbf{k}-\mathbf{k}'). \tag{4}$$

The Green's function $G(E;\mathbf{r},\mathbf{r}')$ must satisfy the equation

$$(H_0-E)G(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}') \tag{5}$$

and is defined by boundary conditions. For the outgoing wave solution of the scattering problem the Green's function reads

$$G^{(+)}(E;\mathbf{r},\mathbf{r}')=\frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty}\frac{\exp[i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')]}{E(k')-[E(k)+i\eta]}d^3k' =\frac{\hbar^2}{2m}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}, \tag{6}$$

where η is an infinitesimal positive constant. The stationary solutions of scattering theory may be written

[1] A good presentation of transport processes is given in the book of F. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960). For thermal conductivity see also the excellent review articles by P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. VII, p. 1; and P. Carruthers, Rev. Mod. Phys. **33**, 92 (1961).

[2] M. Wagner, Phys. Rev. **131**, 1443 (1963).

[3] From now on we designate the localized functions by lower case phi, ϕ or ϕ_j, etc. There should be no confusion with the plane-wave solutions $\phi_{\mathbf{k}}$ which always have the subscript $\mathbf{k}$.

[4] R. G. Newton, Ann. Phys. (N. Y.) **14**, 333 (1961).

[5] E. P. Wigner and L. Eisenbud, Phys. Rev. **72**, 29 (1947).

[6] P. L. Kapur and R. Peierls, Proc. Roy. Soc. (London) **A166**, 277 (1938).

[7] Throughout this paper we shall assume that $\Gamma_j\ll|E_j|$. For small resonance energies, i.e., $E_j\approx\Gamma_j$, it is not clear that a metastable function with the properties (I, II) exists and we have to postpone this question for future investigation. See, however, Wigner (Ref. 8), where the question of resonances for small energies is considered.

[8] E. P. Wigner, Z. Physik **83**, 253 (1933).

in the form of the Lippmann-Schwinger equation

$$\psi_{\mathbf{k}}^{(+)}=\phi_{\mathbf{k}}-G^{(+)}(\mathbf{k})V[1/(1+G^{(+)}(\mathbf{k})V)]\phi_{\mathbf{k}}, \quad (7)$$

where $G^{(+)}$ in the denominator is formally taken as an inverse operator,

$$G^{(+)}(\mathbf{k})=[H_0-(E(\mathbf{k})+i\eta)]^{-1} \quad (8)$$

and the fractional expression is defined by the expansion

$$V[1+G^{(+)}(\mathbf{k})V]^{-1} = V-VG^{(+)}V+VG^{(+)}VG^{(+)}V-+\cdots. \quad (9)$$

This is only a shorthand notation of integrations[9]; for instance,

$$VG^{(+)}V\psi=V(\mathbf{r})\int G^{(+)}(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}')d^3r'. \quad (10)$$

We make now the very important assumption that V is localized within a finite region i,

$$\begin{aligned} V(\mathbf{r})&=V^{(i)}(\mathbf{r}) \quad \text{for} \quad \mathbf{r} \text{ within } i, \\ &=0 \text{ outside}. \end{aligned} \quad (11)$$

Then it is obvious that the expression (9) is also localized in i. In this finite space we can establish the eigenvalue equations

$$\int G^{(+)}(E;\mathbf{r},\mathbf{r}')V(\mathbf{r}')\rho_j(\mathbf{r}')d^3r'=\mu_j(E)\rho_j(\mathbf{r}), \quad (12a)$$

$$\{\mathbf{r},\mathbf{r}' \text{ in } i\}$$

$$\int d^3r'\lambda_i(\mathbf{r}')G^{(+)}(E;\mathbf{r}',\mathbf{r})V(\mathbf{r})=\mu_i(E)\lambda_i(\mathbf{r}). \quad (12b)$$

By transforming both equations to a system of functions which is a complete orthonormal set in the finite region i, and therefore necessarily a discrete (but infinite) set, one can show that for a given E value (a) both equations (12) have only a set of discrete eigenvalues, and that each eigenvalue of one equation is also one of the other, (b) that the functions ρ_j or λ_i, respectively, are independent and each a complete set in the region i, and finally (c) that ρ_j and λ_j are bi-orthogonal and we may normalize them in such a way that

$$\langle\lambda_j^{(i)}|\rho_{j'}^{(i)}\rangle=\int_{(\mathbf{r} \text{ in } i)}\lambda_j(\mathbf{r})\rho_{j'}(\mathbf{r})d^3r=\delta_{jj'}. \quad (13)$$

Recently, equations similar to (12a), and (12b) have been considered by Coester[10]; we refer to this work for a thorough mathematical discussion. Interesting in this context is also the quasiparticle approach of Weinberg,[11] where Eq. (12a) also plays an important role. It is true that one has to define a fixed localization area i for the solution of (12a) and (12b), and one should think that nothing is gained over the Wigner Eisenbud[5] formalism. However, this localization area is *not the localization volume* v of the metastable state [see Eq. (11)]; it can be chosen rather arbitrarily within a certain range without any effect on v whatsoever.

With the projection

$$\phi_{\mathbf{k}}^{(i)}(\mathbf{r})=\sum_j\langle\lambda_j^{(i)}|\phi_{\mathbf{k}}^{(i)}\rangle\rho_j^{(i)}(\mathbf{r}) \quad (14)$$

and the Eqs. (9), (12), (13), we have for (7):

$$\psi_{\mathbf{k}}^{(+)}=\phi_{\mathbf{k}}-G^{(+)}(\mathbf{k})V^{(i)}\sum_j\frac{\langle\lambda_j^{(i)}|\phi_{\mathbf{k}}^{(i)}\rangle}{1+\mu_j(E)}\rho_j^{(i)}, \quad (15)$$

and especially inside the region i:

$$\psi_{\mathbf{k}}^{(+)(i)}=\phi_{\mathbf{k}}^{(i)}-\sum_j\mu_j(E)\frac{\langle\lambda_j^{(i)}|\phi_{\mathbf{k}}^{(i)}\rangle}{1+\mu_j(E)}\rho_j^{(i)}. \quad (15a)$$

Far away from the scattering center, on the other hand, we have

$$\psi_{\mathbf{k}}^{(+)}=\phi_{\mathbf{k}}+(2\pi)^{-3/2}f_{\mathbf{k}}(\Omega)\frac{e^{ikr}}{r} \quad \text{for} \quad r\to\infty, \quad (15b)$$

where

$$f_{\mathbf{k}}(\Omega)=-\left(\frac{\pi}{2}\right)^{1/2}\left(\frac{\hbar^2}{2m}\right)\sum_j\frac{\langle\lambda_j^{(i)}|\phi_{\mathbf{k}}^{(i)}\rangle}{1+\mu_j(E)} \times\int e^{-ik(\mathbf{r}/r)\cdot\mathbf{r}'}V^{(i)}{}_{(\mathbf{r}')}\rho_j^{(i)}(\mathbf{r}')d^3r'. \quad (16)$$

The functions $\rho_j(\mathbf{r})$ and $\lambda_j(\mathbf{r})$ are basic functions to irreducible representations of the point-group $G(V)$ of $V(\mathbf{r})$. But because of the high (accidental) degeneracy of an energy E in the continuum, an eigenfunction of H is not necessarily a basic function to an irreducible representation of $G(V)$. This is directly seen from (15), where the scattering amplitude is a superposition of different basic functions. There are, however, certain energies, for which in a localized region the functional behavior of $\psi_{\mathbf{k}}^{(+)}(\mathbf{r})$ reduces approximately to an irreducible basis of $G(V)$. This is just the scattering resonance and the energy adopts discrete features.

III. SCATTERING RESONANCES

From Eq. (15) we see that the scattering amplitude increases sharply, if one of the denominators approaches zero. The solutions of the equations

$$1+\mu_j(E)=0, \quad E_j<0 \quad (17)$$

give the true localized states. For $E>0$ and localized V there is no true localized eigenstate and μ_j is a complex quantity. In this case we can have at best scattering resonances given by the solutions of the equations

$$1+\mathrm{Re}\mu_j(E)=0, \quad E_j>0. \quad (17a)$$

If the imaginary part of μ_j for the resonance energy E_j is

[9] In the case of a vibrating lattice V and $G^{(+)}$ are matrices and we have matrix products instead of integrations. The integrations on the other hand, can be considered as products of continuous matrices.

[10] F. Coester, Phys. Rev. **133**, B1516 (1964).

[11] S. Weinberg, Phys. Rev. **130**, 776 (1963).

very small, the j term in (15) exceeds all other terms and we have

$$\psi_{\mathbf{k}}^{(+)} \approx \phi_{\mathbf{k}} - \frac{\langle \lambda_j^{(i)} | \phi_{\mathbf{k}}^{(i)} \rangle}{1+\mu_j(E)} G^{(+)}(\mathbf{k}) V^{(i)} \rho_j^{(i)} \quad \text{for} \quad E \to E_j. \tag{18}$$

In the neighborhood of $E=E_j$ we may write

$$1+\mu_j = R_j[E-E_j+i\Gamma_j/2] \tag{19}$$

with the abbreviations

$$R_j = \left.\frac{\partial \operatorname{Re}\mu_j}{\partial E}\right|_{E=E_j}, \quad I_j = \operatorname{Im}\mu_j(E_j), \quad \frac{\Gamma_j}{2} = \frac{I_j}{R_j}. \tag{20}$$

In the region of the scattering center the resonance term in (18) exceeds also the plane-wave term and we have

$$\psi_{\mathbf{k}}^{(+)} \approx -g_j(\Omega_{\mathbf{k}}) \frac{\frac{1}{2}\Gamma_j}{E-E_j+\frac{1}{2}i\Gamma_j} \Phi_j, \tag{21}$$

where

$$\Phi_j(\mathbf{r}) = \int_{(\mathbf{r}' \text{ in } i)} G^{(+)}(E_j; \mathbf{r},\mathbf{r}') \times V^{(i)}(\mathbf{r}') \rho_j^{(i)}(E_j,\mathbf{r}') d^3r', \tag{22}$$

$$g_j(\Omega_{\mathbf{k}}) = (1/R_j)\langle \lambda_j^{(i)} | \phi_{\mathbf{k}}^{(i)} \rangle |_{E=E_j}. \tag{23}$$

The function $\Phi_j(\mathbf{r})$ is a basis in r space for the j representation of the group of V, which is obvious directly from the definition (22). However, it is no localized function, as seen from the asymptotic behavior of $G^{(+)}$, i.e., it cannot be normalized to a finite value. We shall see that $\Phi_j(r)$ has just the fundamental property (I) if we restrict it to a certain normalization volume which is not arbitrary, as was to some extent the region of the eigenvalue equations (12). The function $g_j(\Omega_{\mathbf{k}})$, on the other hand, is a j representation in k space because of the special form of the space group representations $\phi_{\mathbf{k}}$. The resonant scattering amplitude may be written as

$$f_{\mathbf{k}}(\Omega) = -g_j(\Omega_{\mathbf{k}}) \frac{\frac{1}{2}\Gamma_j}{E-E_j+\frac{1}{2}i\Gamma_j} \alpha_j(\Omega), \tag{24}$$

where $\alpha_j(\Omega)$ is a j representation of the group of $V(\mathbf{r})$ in r space,

$$\alpha_j(\Omega) = \left(\frac{\pi}{2}\right)^{1/2} \left(\frac{\hbar^2}{2m}\right) \int e^{-ik_j(\mathbf{r}/r)\cdot\mathbf{r}'} \times V^{(i)}(\mathbf{r}') \rho_j^{(i)}(E_j,\mathbf{r}') d^3r'. \tag{25}$$

It will be shown that the functions $g_j(\Omega_{\mathbf{k}})$ and $\alpha_j(\Omega)$ exhibit some very interesting properties, which simplify the calculation.

We have to emphasize that the formulas (18) and (24) are only valid if the resonance is nondegenerate, i.e., if the representation j is one-dimensional. For degenerate resonances we have to sum up over all eigenfunctions $[\lambda_j,\rho_j]$ belonging to the same eigenvalue μ_j. As this generalization is obvious, we shall confine the following consideration to nondegenerate resonances.

Three restrictive remarks are necessary. (1) The second term in (15), exact as it stands, is normally not a sum of pure resonance terms, but may be decomposed into a nonresonant term, often called "potential scattering," and a sum of resonance terms. We refer in this context to the fundamental paper by Wigner.[12] Therefore, Eq. (24) has to be supplemented by the potential-scattering term; but the term is often negligible. (2) If $V \leqq 0$ everywhere, the plane-wave term in (18) has the same order of magnitude as the resonance term, whence it cannot be neglected near the resonance, as done in Eq. (21). (3) If the energetic distance between the resonances E_j is of the order of Γ_j, the "one-level" formula (21) is inadequate and the neighboring resonances have to be included. We refer to another paper by Wigner,[13] where this question is discussed.

It is apparently not difficult to incorporate these modifications into the subsequent formalism, but for clarity we avoid this extension, the more so, as the exact definition of metastable states in the Krylov-Fock formalism (Sec. VII) is not changed by them.

IV. RESONANT SCATTERING OF A WAVE PACKET

The metastable functions are found in a most natural way by investigating the time behavior of a wave packet. If there is a scattering resonance, a part of the wave packet will be captured at the scattering center, whereas the residual part moves approximately as if no scattering center were present. The captured part decays slowly and dissipates away from the scatterer. This process is well known and described in standard literature.[14] We shall modify the treatment to meet our special intentions.

We consider a wave packet of the general form:

$$\Psi(\mathbf{r},t) = \int_{\Delta E} C(\mathbf{k}) \psi_{\mathbf{k}}^{(+)}(\mathbf{r}) e^{-iEt/\hbar} d^3k \tag{26}$$

and assume its energy width to be much larger than the resonance,

$$\Delta E \gg \Gamma_j, \tag{27}$$

but small enough to cover only one resonance. Capture of a part of the packet will only occur, if its projection onto a j representation is not zero. Consequently, we make the choice

$$C(\mathbf{k}) = C_0 \frac{g_j^*(\Omega_{\mathbf{k}})}{\langle g_j | g_j \rangle} \quad \text{for} \quad E_j - \frac{\Delta E}{2} < E < E_j + \frac{\Delta E}{2}, \tag{28}$$
$$= 0 \quad \text{otherwise},$$

[12] E. P. Wigner, Phys. Rev. **70**, 15 (1946).
[13] E. P. Wigner, Phys. Rev. **70**, 606 (1946).
[14] For example, E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), pp. 129, 240; A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1961), Vol. I, Chap. X, p. 401 ff.

where the abbreviation has been used

$$\langle g_j | g_j \rangle = \int g_j(\Omega_k) g_j^*(\Omega_k) d\Omega_k . \tag{29}$$

By means of the general expression (15) and the definition of g_j [Eq. (23)] it is easily realized that with the choice (28) the wave packet (26) is just a basic function to the irreducible representation j of $G(V)$. Let us first calculate that part of $\Psi(\mathbf{r},t)$ which belongs to the plane wave part of $\psi_k^{(+)}$,

$$\Psi_0(\mathbf{r},t) = \int_{\Delta E} C(\mathbf{k}) \phi_k(\mathbf{r}) e^{-iEt/\hbar} d^3k . \tag{30}$$

For large distances from the scattering center $\Psi_0(\mathbf{r},t)$ takes the rather simple form

$$\underset{(r\to\infty)}{\Psi_0}(\mathbf{r},t) \approx \frac{1}{(2\pi)^{3/2}} \frac{k_j^2}{\langle g_j | g_j \rangle} \frac{e^{-iE_j t/\hbar}}{r} \times \left\{ e^{-ik_j r} g_j(-\Omega) \frac{\sin[(\Delta E/4E_j)(k_j r + 2E_j t/\hbar)]}{[k_j r + 2E_j t/\hbar]} - e^{+ik_j r} g_j(\Omega) \frac{\sin[(\Delta E/4E_j)(k_j r - 2E_j t/\hbar)]}{[k_j r - 2E_j t/\hbar]} \right\}, \tag{31}$$

where we have assumed the region ΔE to be small enough (but $\gg \Gamma_j$) to allow a linear approximation $k = k_j + (k_j/2E_j)(E - E_j)$; $(-\Omega)$ is the space direction belonging to $(-\mathbf{r})$. As the formula applies for large r values, one realizes that the first term characterizes the motion for $t<0$, the second for $t>0$; for $t<0$ (31) is a centrally symmetric incoming wave, for $t>0$ an outgoing one. The center of $\Psi_0(r,t)$ is given by

$$r_c = -(2E_j/\hbar k_j)t \quad \text{for} \quad t<0, \tag{32a}$$

$$r_c = +(2E_j/\hbar k_j)t \quad \text{for} \quad t>0, \tag{32b}$$

and the mean radial extension

$$\Delta r = (8\pi/k_j)(E_j/\Delta E) . \tag{33}$$

Extrapolating the behavior (32a,b) we see that the center of $\Psi_0(r,t)$ is at $t=0$ just in the region of the scatterer. The part of $\Psi(\mathbf{r},t)$ which belongs to the scattering amplitude of $\psi_k^{(+)}$ is also easily calculated for large r, using (15b),

$$\underset{(r\to\infty)}{\Psi_s}(\mathbf{r},t) = (2\pi)^{-3/2} \int_{\Delta E} C(\mathbf{k}) f_k(\Omega) \frac{e^{ikr}}{r} e^{-iEt/\hbar} d^3k \tag{34}$$

and inserting (24) and (28),

$$\underset{(r\to\infty)}{\Psi_s}(\mathbf{r},t) \approx +i(2\pi)^{-1/2} C_0 k_j^3 \frac{\Gamma_j}{4E_j} \frac{\alpha_j(\Omega)}{r} e^{i(k_j r - E_j t/\hbar)} \left\{ \exp\left[-\left(\frac{t}{\hbar} - \frac{k_j r}{2E_j} \right) \frac{\Gamma_j}{2} \right] \times \begin{cases} 0 & \text{for} \quad t<0 \\ 1 & \text{for} \quad r<2E_j t/\hbar k_j \\ 0 & \text{for} \quad r>2E_j t/\hbar k_j \end{cases} \right.$$

$$\left. - \frac{1}{\pi} \mathrm{Si}\left[\frac{\Delta E}{2} \left| \frac{t}{\hbar} - \frac{k_j r}{2E_j} \right| \right] \times \begin{cases} 1 & \text{for} \quad t/\hbar > k_j r/2E_j \\ -1 & \text{for} \quad t/\hbar < k_j r/2E_j \end{cases} \right\}. \tag{35}$$

Here again a linear approximation for k has been used in the region ΔE. The first term describes just the dissipation of that part of the packet which has been captured at $t=0$ and is slowly re-emitted. For $t>0$ the second term is a wave packet similar to $\Psi_0(\mathbf{r},t)$ with its center at $r_c = 2E_j t/\hbar k_j$; for $t<0$ there is no center, and it is evident that this term represents the subtraction from $\Psi_0(\mathbf{r},t)$ to account for the loss by capture. Redefine now

$$\underset{(r\to\infty)}{\Psi_0'}(\mathbf{r},t) = \Psi_0(\mathbf{r},t) - \frac{i}{(2\pi)^{3/2}} C_0 k_j^3 \frac{\Gamma_j}{2E_j} \frac{\alpha_j(\Omega)}{r} e^{i(k_j r - E_j t/\hbar)} \mathrm{Si}\left[\frac{\Delta E}{2} \left| \frac{t}{\hbar} - \frac{k_j r}{2E_j} \right| \right] \times \begin{cases} 1 & \text{for} \quad t/h > k_j r/2E_j \\ -1 & \text{for} \quad t/h < k_j r/2E_j \end{cases}. \tag{36a}$$

For $t>0$ this is just the part $\Delta\Psi(t)$ of Eq. (1) which moves as if no scattering center were present. Further

$$\underset{(r\to\infty)}{\Psi_s'}(\mathbf{r},t) = \frac{i}{(2\pi)^{1/2}} C_0 k_j^3 \frac{\Gamma_j}{4E_j} \frac{\alpha_j(\Omega)}{r} \exp\{ i(k_j r - E_j t/\hbar) - (\Gamma_j/2)[t/\hbar - (k_j r)/2E_j] \} \times \begin{cases} 0 & \text{for} \quad t<0, \\ 1 & \text{for} \quad r<2E_j t/\hbar k_j, \\ 0 & \text{for} \quad r>2E_j t/\hbar k_j \end{cases} \tag{36b}$$

and be $\Psi^{lc}(\mathbf{r},t)$ the part of Ψ which is localized in the scattering region after capture. Then we must clearly have:

$$\langle \Psi^{lc}(0) | \Psi^{lc}(0) \rangle = \lim_{t\to-\infty} \langle \Psi_0'(t) | \Psi_0'(t) \rangle - \lim_{t\to+\infty} \langle \Psi_0'(t) \Psi_0'(t) \rangle \tag{37}$$

and also:

$$\langle \Psi^{lc}(0) | \Psi^{lc}(0) \rangle = \lim_{t\to+\infty} \langle \Psi_s'(t) | \Psi_s'(t) \rangle . \tag{38}$$

These are two normalization conditions for $\Psi^{lc}(0)$. They will allow us to define the localization volume of the metastable function. Inserting (36b) into (38) we get:

$$\langle\Psi^{lc}(0)|\Psi^{lc}(0)\rangle=\frac{1}{8\pi}|C_0|^2k_j{}^5\left(\frac{\Gamma}{2E_j}\right)\langle\alpha_j|\alpha_j\rangle, \tag{38a}$$

where

$$\langle\alpha_j|\alpha_j\rangle=\int\alpha_j(\Omega)\alpha_j{}^*(\Omega)d\Omega. \tag{39}$$

Identifying both equations (37) and (38) we get the relation

$$\lim_{t\to+\infty}\langle\Psi_s{}'(t)|\Psi_s{}'(t)\rangle=(\lim_{t\to-\infty}-\lim_{t\to+\infty})\langle\Psi_0{}'(t)|\Psi_0{}'(t)\rangle. \tag{40}$$

or inserting the respective expressions we find the condition

$$\mathrm{Im}\int g_j(\Omega)\alpha_j{}^*(\Omega)d\Omega=2k_j\langle\alpha_j|\alpha_j\rangle\langle g_j|g_j\rangle. \tag{41}$$

V. METASTABLE FUNCTIONS

In the preceding section we have only considered the region at large distances from the scattering center. Let us now investigate the scattering region itself. We have shown already that the introduced wave packet is localized near the scattering region at $t=0$. The eigensolution $\psi_k{}^{(+)}$ for this region is given by (21) and we may write therefore for the captured part of our wave packet

$$\Psi^{lc}(\mathbf{r},t)=-\int_{\Delta E}C(\mathbf{k})g_j(\Omega_k)\frac{\Gamma_j/2}{E-E_j+i\Gamma_j/2}\Phi_j(\mathbf{r})e^{-Et/\hbar}d^3k \tag{42}$$

and this is approximately

$$\Psi^{lc}(\mathbf{r},t)\approx+i\pi C_0\Phi_j(\mathbf{r})k_j{}^3\frac{\Gamma_j}{2E_j}\exp[-iE_jt/\hbar-\Gamma_jt/2\hbar]\begin{cases}1 & \text{for } t>0,\\ 0 & \text{for } t<0.\end{cases} \tag{43}$$

This important formula indicates that the functional form of the captured wave does not change in time, whereas the amplitude decreases exponentially. This is just the fundamental property of a metastable function as postulated in (I). Yet, in Sec. III we have seen already that Φ_j cannot be normalized to a finite value without restriction to a finite space region. On the other hand, $\psi(\mathbf{r},0)$ has to be normalized to the value (38a), and this allows us to define the localization volume v of the metastable function

$$\int_v\Phi_j(\mathbf{r})\Phi_j{}^*(\mathbf{r})d^3r=\frac{1}{(2\pi)^3}\left(\frac{2E_j}{\Gamma_jk_j}\right)\langle\alpha_j|\alpha_j\rangle \tag{44}$$

and we establish

$$\begin{aligned}\phi_j(\mathbf{r})&\equiv\Phi_j(\mathbf{r})\text{ within }v,\\ &\equiv 0\text{ outside}.\end{aligned} \tag{45}$$

An alternative definition is given by Kemble[15] who suggested the introduction of a localization function

$$\rho=\exp(-\sigma r^n), \tag{46}$$

where n is a positive integer ≥ 2 to ascertain that ρ is practically unity inside the scattering region yet approaches zero rather rapidly outside. Then we may write

$$\phi_j(\mathbf{r})=\rho\Phi_j(\mathbf{r}), \tag{47}$$

where σ is determined by the equation

$$\langle\rho\Phi_j|\rho\Phi_j\rangle=\frac{1}{(2\pi)^3}\left(\frac{2E_j}{\Gamma_jk_j}\right)\langle\alpha_j|\alpha_j\rangle. \tag{44a}$$

Thus the investigation of a suitably chosen wave packet has given us both the functional definition and the localization volume of the metastable function ϕ_j. We shall see that this is not the only way, but that other procedures lead to the same result.

VI. PROJECTION ONTO THE SCATTERING STATES

There is one other way to determine the normalization of $\phi(\mathbf{r})$ which is not based on the discussion of a wave packet. This is achieved by projecting ϕ_j onto the scattering eigenfunctions $\psi_k{}^{(+)}$ and is suggested by the fact that all $\psi_k{}^{(+)}$ near the resonance $E=E_j$ and within the scattering region have the same functional behavior given by $\Phi_j(r)$ [see Eq. (21)].

[15] E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (Dover Publications, Inc., New York, 1937), p. 190.

We make the *assumption*

$$\phi_j \equiv \Phi_j(\mathbf{r}) \text{ within } v, \quad \equiv 0 \text{ outside}, \tag{A}$$

and it is to be emphasized that this is now rather a postulate than a result as in (45). Taking it as such, we have (a) to prove that it is in agreement with relation (I) and (b) to determine the localization area v.

Let us represent ϕ_j as

$$\phi_j(\mathbf{r}) = \int A_j(\mathbf{k}) \psi_{\mathbf{k}}^{(+)}(\mathbf{r}) d^3k. \tag{48}$$

Then by means of (A) and (21)

$$A_j(\mathbf{k}) = -g_j^*(\Omega_{\mathbf{k}}) \frac{(\Gamma_j/2)}{E - E_j - i\Gamma_j/2} \langle \phi_j | \phi_j \rangle. \tag{49}$$

Now from (48):

$$\langle \phi_j | \phi_j \rangle = \int A_j(\mathbf{k}) A_j^*(\mathbf{k}) d^3k, \tag{50}$$

and inserting (49):

$$= \langle g_j | g_j \rangle (\Gamma_j k_j / 2E_j) \tfrac{1}{2}\pi k_j^2 [\langle \phi_j | \phi_j \rangle]^2,$$

or

$$(\Gamma_j k_j / 2E_j) \tfrac{1}{2}\pi k_j^2 \langle g_j | g_j \rangle \langle \phi_j | \phi_j \rangle = 1, \tag{51}$$

which is again a normalization condition for ϕ_j and determines v. If the definition of ϕ_j is unique, both relations (44) and (51) have to be identical, whence we arrive at

$$(k_j^2/(4\pi)^2) \langle \alpha_j | \alpha_j \rangle \langle g_j | g_j \rangle = 1. \tag{52}$$

This condition is indeed satisfied and a consequence of the stationariness condition for the $\psi_{\mathbf{k}}^{(+)}$, which can be written as

$$\frac{2}{r^2} \int f_{\mathbf{k}}(\Omega) f_{\mathbf{k}}^*(\Omega) d\Omega = -\left\{ \frac{e^{-ikr}}{r} \int f_{\mathbf{k}}^*(\Omega) e^{i\mathbf{k}\cdot\mathbf{r}} [1 + \cos\theta] d\Omega + \text{c.c.} \right\}, \tag{53}$$

where c.c. is the complex conjugate. Consider, for example, the simple case of an s-type scattering,[16]

$$f_{\mathbf{k}}(\Omega) = -\frac{1}{k} \frac{\Gamma/2}{E - E_0 + i\Gamma/2}. \tag{54}$$

Inserting that into the right-hand side of (53) and using definition (24) for $f_{\mathbf{k}}(\Omega)$ we find

$$g_j(\Omega_k) g_j^*(\Omega_k) \langle \alpha_j | \alpha_j \rangle = 4\pi/k_0^2, \tag{55}$$

or

$$\langle g_j | g_j \rangle \langle \alpha_j | \alpha_j \rangle = (4\pi/k_0)^2 \tag{55a}$$

as required by (52).

[16] E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), p. 238.

Finally we have to show that ϕ_j is of the form (I), but this is easily demonstrated. Using (48), (49), (21), and (51) one has

$$\phi_j(t) = \int A_j(\mathbf{k}) \psi_{\mathbf{k}}^{(+)}(\mathbf{r}) e^{-iEt/\hbar} d^3k$$

$$= \frac{k_j^3}{2E_j} \langle g_j | g_j \rangle \langle \phi_j(0) | \phi_j(0) \rangle \phi_j(0) \times \int \frac{(\Gamma_j/2)^2}{(E - E_j)^2 + \Gamma_j^2/4} e^{-iEt/\hbar} dE$$

$$= \phi_j(0) \exp[-iE_j t/\hbar - \Gamma_j t/2\hbar]. \tag{56}$$

VII. EXTENSION OF THE KRYLOV-FOCK FORMALISM

In both preceding definitions of the metastable state we have adopted the knowledge of the relation (21) and assumed its validity in the whole region of ϕ_j. An approach which is not based on this knowledge can be taken in close analogy to the theory of Krylov and Fock.[17] They show that in the one-dimensional space the postulates (I) and (II) suffice to fix the coefficients $A_j(\mathbf{k})$ up to a normalization factor. Extending their method to three-dimensional space one can determine $A_j(\mathbf{k})$ up to a function $G_j(\Omega_k)$ on the surface $E(\mathbf{k}) = E_j$. Using the expansion (48) and its progress in time we can write the projection of $\phi_j(t)$ onto $\phi_j(0)$ as

$$\langle \phi_j(t) | \phi_j(0) \rangle = \int A_j(\mathbf{k}) A_j^*(\mathbf{k}) e^{-iEt/\hbar} d^3k. \tag{57}$$

But this projection can also be written by using the two postulates (I) and (II),

$$\langle \phi_j(t) | \phi_j(0) \rangle = \exp[-iE_j t/\hbar - \Gamma_j t/2\hbar] \times \langle \phi_j(0) | \phi_j(0) \rangle. \tag{58}$$

Thus we get

$$\exp[-iE_j t/\hbar - \Gamma_j t/2\hbar] \langle \phi_j(0) | \phi_j(0) \rangle = \int A_j(\mathbf{k}) A_j^*(\mathbf{k}) e^{-iEt/\hbar} d^3k \tag{59}$$

and it is easily seen that this can be inverted to yield

$$\left(\frac{k^3}{2E} \right) \int A_j(\mathbf{k}) A_j^*(\mathbf{k}) d\Omega_{\mathbf{k}} = \langle \phi_j(0) | \phi_j(0) \rangle \frac{(\Gamma_j/2\pi)}{(E - E_j)^2 + (\Gamma_j/2)^2}. \tag{60}$$

To solve this equation we try the ansatz

$$A_j(\mathbf{k}) = G_j(\Omega_{\mathbf{k}}) a_j(E), \tag{61}$$

[17] N. S. Krylov and W. A. Fock, Zh. Eksperim. i Teor. Fiz. **17**, 93 (1947). A good review of this work is given in D. F. Blochinzew, *Grundlagen der Quantenmechanik* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1953).

which implies

$$a_j(E)a_j^*(E) = \frac{\langle\phi_j(0)\,|\,\phi_j(0)\rangle}{\langle G_j\,|\,G_j\rangle}\left(\frac{E\Gamma_j}{k^3}\right)\frac{1}{(E-E_j)^2+(\Gamma_j/2)^2} \quad (62)$$

and as $\phi_j(t)=0$ for $t<0$

$$a_j(E)=\left[\frac{\langle\phi_j(0)\,|\,\phi_j(0)\rangle}{\langle G_j\,|\,G_j\rangle}\left(\frac{E\Gamma_j}{k^3}\right)\right]^{1/2}\frac{1}{(E-E_j)-i\Gamma_j/2}, \quad (63)$$

which is just the energetic behavior of the preceding $A(\mathbf{k})$'s. $\langle G_j\,|\,G_j\rangle$ is of finite value. It is clear that we cannot calculate G_j by this formalism without involving some further knowledge of the scattering solutions $\psi_k^{(+)}$. But whatever the functional form of $G_j(\Omega_k)$ may be, it is clear (because the derivation was based on the presupposition) that

$$\phi_j \sim \int G_j(\Omega_k)\frac{1}{(E-E_j)-i\Gamma_j/2}\psi_k^{(+)}d^3k \quad (64)$$

is a localized function. Therefore, (64) is a definition of the quasilocalized state which does not require the restriction to a special localization area v. This is the principal advantage of the method of Krylov and Fock. But this advantage is of no practical importance, because in order to use (64) we would have to know the $\psi_k^{(+)}$ especially in the intermediate space region where it decreases from large values to small ones; this decrease is fairly well approximated by (21), but while ϕ_j approaches zero, (21) breaks down, and we have to use a complicated expression for $\psi_k^{(+)}$ in a region where ϕ_j is already practically zero. To avoid this we can use the approximation (21) within a restricted well-defined space region v, while putting $\phi_j=0$ outside, and we are back to the formulation of the last section.

VIII. FURTHER PROPERTIES OF $g_j(\Omega_k)$ AND $\alpha_j(\Omega)$

In Sec. VI we have made the presupposition that ϕ_j be zero outside v and subsequently derived the result (49). Let us now check directly if this result agrees with (A) by using (15b) and (24) for the region outside v

$$\left.\frac{\phi_j(\mathbf{r})}{\langle\phi_j\,|\,\phi_j\rangle}\right|_{r\to\infty} = -(2\pi)^{-3/2}\int g_j^*(\Omega_k)\frac{\Gamma_j/2}{E-E_j-i\Gamma_j/2}e^{ik\cdot r}d^3k+(2\pi)^{-3/2}\frac{\alpha_j(\Omega)}{r}\langle g_j\,|\,g_j\rangle\left(\frac{\Gamma_j}{2}\right)^2\int\frac{e^{ikr}}{(E-E_j)^2+(\Gamma_j/2)^2}dk,$$

$$= (2\pi)^{-1/2}\frac{1}{r}\left(\frac{\Gamma_j k_j^2}{4E_j}\right)\exp[ik_jr-k_j\Gamma_jr/4E_j]\{-2\pi g_j^*(\Omega)+\tfrac{1}{2}k_j\alpha_j(\Omega)\langle g_j\,|\,g_j\rangle\}. \quad (65)$$

This is zero only if

$$g_j^*(\Omega) = (k_j/4\pi)\langle g_j\,|\,g_j\rangle\alpha_j(\Omega). \quad (66)$$

We get the very interesting result that $g_j^*(\Omega)$ and $\alpha_j(\Omega)$ have the same functional form. Multiplying (66) by g_j and integrating over the surface we come back to the Eq. (51).

It is worthwhile to note that (66) is in agreement with the *optical theorem*[18]

$$\int f_k(\Omega)f_k^*(\Omega)d\Omega = (4\pi/k)\,\mathrm{Im}f_k(\Omega_k), \quad (67)$$

which reads for $E=E_j$, using (24)

$$g_j(\Omega_k)g_j^*(\Omega_k)\langle\alpha_j\,|\,\alpha_j\rangle = (4\pi/k_j)\,\mathrm{Re}g_j(\Omega_k)\alpha_j(\Omega_k). \quad (67a)$$

This is an identity if we insert the relation (66). There is still another way of checking (66), if we calculate the dissipation of ϕ_j:

$$\left.\frac{\phi_j(t)}{\langle\phi_j(0)\,|\,\phi_j(0)\rangle}\right|_{r\to\infty} = 0 \quad \text{for} \quad \frac{k_jr}{2E_j} > \frac{t}{\hbar},$$

$$= (2\pi)^{-1/2}\frac{\Gamma_jk_j^3}{8E_j}\frac{\alpha_j(\Omega)}{r}\langle g_j\,|\,g_j\rangle\exp\left[ik_jr-\frac{iE_jt}{\hbar}+\frac{\Gamma_j}{2}\left(\frac{k_jr}{2E_j}-\frac{t}{\hbar}\right)\right] \quad \text{for} \quad \frac{k_jr}{2E_j} < \frac{t}{\hbar},$$

whence, inserting (66) and integrating,

$$\frac{\langle\phi_j(t)\,|\,\phi_j(t)\rangle|_{\text{out}}}{\langle\phi_j(0)\,|\,\phi_j(0)\rangle} = 1-e^{-\Gamma_jt/\hbar}. \quad (68)$$

This is just the behavior which is required by the localized time property I and conservation of probability.

IX. SUMMARY AND DISCUSSION

We may summarize the result in the following way: A metastable state is characterized by a time-independ-

[18] E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), p. 499.

ent functional form and a time-dependent decay factor. These properties are only possible within a restricted space region whence the metastable function is zero outside this region. The general expression for such a behavior is given by its scattering expansion at $t=0$

$$\text{(a)} \qquad \phi_j(0)=-\int g_j^*(\Omega_k)\frac{\Gamma_j/2}{E-E_j-i\Gamma_j/2}\psi_k^{(+)}d^3k\,,$$

where $\Gamma_j/2$ is the decay constant and E_j the energy of the metastable state.

Each metastable state is connected with a scattering resonance and is a basis for an irreducible representation of the group of the scattering potential. In the neighborhood of a resonance the scattering amplitude is of the form

$$\text{(b)} \qquad f_k(\Omega)=-g_j(\Omega_k)\frac{\Gamma_j/2}{E-E_j+i\Gamma_j/2}\alpha_j(\Omega)$$

and the scattering solution within the scattering region,

$$\text{(c)} \qquad \psi_k^{(+)}(\mathbf{r})\approx -g_j(\Omega_k)\frac{\Gamma_j/2}{E-E_j+i\Gamma_j/2}\Phi_j(\mathbf{r})\,,$$

where g_j, α_j, and Φ_j are given by (23), (25), and (22), respectively. We have shown that α_j and g_j have the property

$$\text{(d)} \qquad g_j^*(\Omega)=k_j/4\pi\langle g_j|g_j\rangle\alpha_j(\Omega)$$

and ϕ_j, as defined by (a), is normalized to the value

$$\text{(e)} \qquad \langle\phi_j(0)|\phi_j(0)\rangle=\frac{1}{(2\pi)^3}\frac{2E_j}{\Gamma_j k_j}\langle\alpha_j|\alpha_j\rangle.$$

For practical purposes (a) is of little utility, because it is necessary to employ the exact eigenfunctions $\psi_k^{(+)}$ in a region where ϕ_j is already small, in order to ensure the the decrease to zero, whereas in the region of the validity of (c) we have $\phi_j=\Phi_j$. Therefore, it is useful to define

$$\text{(f)} \qquad \begin{aligned}\phi_j&\equiv\Phi_j \text{ within } v\,,\\ &\equiv 0 \text{ outside}\,,\end{aligned}$$

and determine v by the normalization condition (e).

We have checked our established concept of a metastable function in several different ways and shown that it is consistent and in agreement with other general results of scattering theory. The important result is that it has been possible to give a general definition of a metastable state, without referring to a special model. It also has not been necessary to introduce a "localizing" Hamiltonian H_0', which is identical with the true one within the scattering region, but with an altered asymptotic behavior to ensure truly localized eigenfunctions. The choice of such a Hamiltonian is evidently not free from arbitrariness.

To avoid arbitrariness one has to look for a general property which a metastable should exhibit in any case. There is only one property of such general nature: that it should differ from a true stable state only by an exponential decay factor in time, i.e., there should be apart from it a periodic time factor and a constant functional form. We have introduced this as the only fundamental postulate for the definition of a metastable state. (The localization to a finite space area is already a consequence of it.) Using this postulate and scattering theory, it is straightforward to calculate the metastable function, either by considering the captured part of a wave packet, or by projecting the supposed function directly onto the system of scattering solutions.

Although the concept of metastable states, as defined by the extended Krylov-Fock formalism, is an exact one, the difficulty in the general investigation lies in the fact that one has to use approximations for almost each single calculation which are all permissible only if

$$\Gamma_j \ll E_j.$$

When the scattering resonance gets broader, the metastable state, given by the fundamental postulate (I), decays quickly and the clear physical features fade away.

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