Response of hybridized (mixed valence) systems to external probes

C. E. T. Gonçalves da Silva* and L. M. Falicov†

Instituto de Fisica "Gleb Wataghin," Universidade Estadual de Campinas, 13.100 Campinas, SP, Brasil
and Department of Physics,‡ University of California, Berkeley, California 94720
(Received 11 August 1975)

The problem of the response of a hybridized system to an external probe is discussed from a completely quantum-mechanical point of view. An exactly soluble model, which describes qualitatively the mixed-valence states of rare-earth compound solids, is presented. We show that it is possible to obtain regimes of "single response"—e.g., isomer shifts—as well as regimes of "two responses"—e.g., photoelectron emission spectra. The calculation does not involve real time fluctuations. We point out that it would be worthwhile to investigate experimentally intermediate regimes where the characteristic energy of the probe is comparable to the energy separation of the hybridized states.

I. INTRODUCTION AND FORMULATION

Hybridized systems are a common occurrence in nature. The phenomenon, known for a long time to quantum chemists as configuration interaction, orbital hybridization, etc., has gained renewed interest among physicists lately because of the spectacular properties exhibited by some rare-earth solid compounds, in particular cerium metal[1] and the samarium salts.[2,3]

In these compounds it is found that the number of $4f$ electrons is not a good quantum number for describing the ground state.[4,5] The $4f$ electrons are on the other hand strongly correlated among themselves—they cannot be treated as itinerant Bloch electrons—and this results in solids in which only two configurations, say $(4f)^n$ and $(4f)^{n+1}$, coexist in the ground state. Such a state is known as a state of mixed valence.

Many properties of the rare-earth solids are strongly dependent on the number of $4f$ electrons. In particular lattice parameters,[3] magnetic susceptibility,[6] photoelectron emission spectra,[7] hyperfine spectra,[8] isomer shifts,[9] and transport properties[10] are, among others, sensitive functions of the rare-earth–ion valence. Experimentally it is found that certain properties, e.g., lattice parameters and isomer shifts, yield results which are intermediate between the two valences, i.e., a weighted *average* between the values which correspond to the pure $(4f)^n$ and the pure $(4f)^{n+1}$ configurations. In contraposition other experiments, e.g., photoelectron emission spectra, yield not an average but a *superposition* of the results obtained from each of the pure configurations.

The two different behaviors have led to some confusion in the interpretation of the data and in the understanding of the nature of the ground state. It is also the reason for the misleading introduc-

tion in the literature of the word "fluctuation" when refering to some properties of the ground state.

We present in this paper a very simple conceptual model, which can be solved exactly, and which clearly illustrates the essential physical aspects of the problem. The model system consists of:

(a) An electronic system with two quantum states, $|a\rangle$ and $|b\rangle$, such that in the absence of hybridization they have energies E_a and E_b (we choose $E_a \leq E_b$):

$$H_e = E_a |a\rangle\langle a| + E_b |b\rangle\langle b| . \tag{1}$$

(b) A hybridization term which mixes $|a\rangle$ and $|b\rangle$:

$$H_h = V(|a\rangle\langle b| + |b\rangle\langle a|) . \tag{2}$$

By a proper choice of phases we have made V a real positive quantity $(V \geq 0)$.

(c) An outside probe, which we take to be a harmonic oscillator of creation and destruction operators $c^\dagger$ and c, respectively, which has a characteristic frequency ω_a when the electronic system is in state $|a\rangle$, and a frequency ω_b when the electronic system is in state $|b\rangle$:

$$H_{\text{osc}} = (\hbar\omega_a |a\rangle\langle a| + \hbar\omega_b |b\rangle\langle b|)c^\dagger c . \tag{3}$$

(d) The total Hamiltonian is now

$$H = H_e + H_h + H_{\text{osc}} . \tag{4}$$

It is evident that $N_c \equiv c^\dagger c$ commutes with the Hamiltonian and the number of oscillator quanta is a good quantum number. For each value of N_c there are two eigenstates of the total system which can be obtained by straightforward diagonalization of a (2×2) matrix. These states can be labeled $|N_c\alpha\rangle$ and $|N_c\beta\rangle$, chosen so that $E(N_c\alpha) \leq E(N_c\beta)$. The ground state of the system is therefore $|0\alpha\rangle$.

This ground state $|0\alpha\rangle$ is coupled by the outside

probe—the harmonic oscillator—to two states:
$|1\alpha\rangle$ and $|1\beta\rangle$ with two characteristic frequencies
ω_α and ω_β,

$$\hbar\omega_\alpha = E(1\alpha) - E(0\alpha),$$

$$\hbar\omega_\beta = E(1\beta) - E(0\alpha), \tag{5}$$

with oscillator strengths given by

$$f_\alpha = |\langle 1\alpha | c^\dagger | 0\alpha \rangle|^2,$$

$$f_\beta = |\langle 1\beta | c^\dagger | 0\alpha \rangle|^2. \tag{6}$$

For this model system we can study exactly several features which are common to this and to real (many-body) systems. These include initial- and final-state configuration interactions and non-orthogonality of ground and excited states. We may also examine a full range of orders of magnitude for the relevant parameters. So, although the model is extremely simple and the formalism elementary, there are many "regimes" in which we obtain qualitatively distinct results. These results are presented and discussed in Sec. II.

II. RESULTS AND DISCUSSION

In order to study the various regimes we define the following dimensionless parameters.

$$x \equiv \frac{E_b - E_a}{\hbar |\omega_b - \omega_a|} \geq 0; \tag{7}$$

$$y \equiv \frac{2V}{\hbar |\omega_b - \omega_a|} \geq 0; \tag{8}$$

$$z \equiv \frac{\omega_b - \omega_a}{|\omega_b - \omega_a|} = \pm 1. \tag{9}$$

The results for the frequencies of the coupled system are expressed as

$$\omega_{\alpha,\beta} = \tfrac{1}{2}(\omega_a + \omega_b) + \tfrac{1}{2}|\omega_b - \omega_a| \nu_{\alpha,\beta}. \tag{10}$$

We distinguish the two cases $z = +1$ and $z = -1$ and present the results in Fig. 1 and Tables I and II. In Fig. 1 we plot the response frequencies (arbitrary units) for states α and β and the respective oscillator strengths using the values given in Tables I and II for ν_α, f_α, ν_β, and f_β. The analysis of the results shows the following interesting features:

(i) The low-frequency ν_α is such that

$$-1 \leq \nu_\alpha \leq 1,$$

so that ω_α is always between ω_a and ω_b. The high-frequency ν_β is such that $\nu_\beta \geq 1$, i.e., ω_β is larger than both ω_a and ω_b.

(ii) Whenever $\omega_\beta \gg \omega_a, \omega_b$, the oscillator strength f_β associated with it is very small.

(iii) A special case of (ii) occurs when

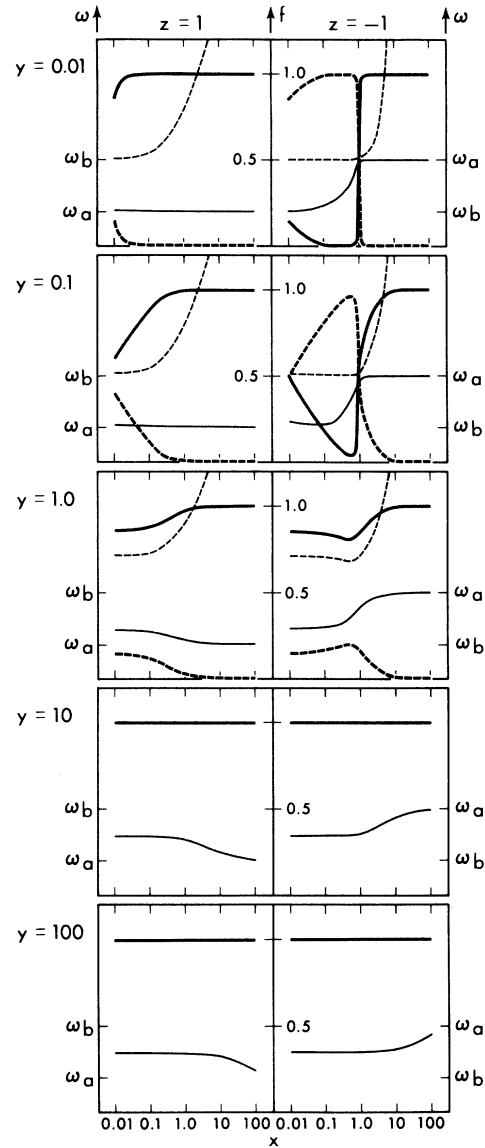$$E_b - E_a \gg \hbar |\omega_b - \omega_a| \quad \text{and} \quad E_b - E_a > 2V;$$

FIG. 1. Frequencies and oscillator strengths of the coupled system. The left-hand side shows the results for $z = 1$ $(\omega_b > \omega_a)$ and the right-hand side, the results for $z = -1$ $(\omega_b < \omega_a)$. Values of the hybridization parameter y are indicated on the left part of the figure. The energy separation between the electronic levels x is plotted on a logarithmic scale at the bottom of the figure. The ordinates are the response frequencies in arbitrary units (extreme left and extreme right) and the oscillator strength (center). The response frequencies are indicated by the thin solid and dashed lines. The oscillator strengths are indicated by the thick solid and dashed lines. The solid lines are associated with state α, the dashed lines with state β. Note that for $y = 10.0$ and $y = 100.0$, the response frequencies for state β are outside the scale of the picture and the respective oscillator strengths are completely negligible (see text for a more complete discussion).

TABLE I. Frequencies ν and oscillator strengths f for $z=1$ $(\omega_b > \omega_a)$. [a]

		$y=0$	$y=0.01$	$y=0.1$	$y=1$	$y=10$	$y=100$
$x=0$		-1	-0.990	-0.905	-0.414	-0.050	-0.005
		?	0.505	0.550	0.854	0.998	1.000
		$+1$	1.010	1.105	2.414	20.05	200.0
		?	0.495	0.450	0.146	2×10^{-3}	2×10^{-5}
$x=0.01$		-1	-0.996	-0.914	-0.421	-0.051	-0.015
		1	0.857	0.599	0.855	0.998	1.000
		1.02	1.024	1.115	2.421	20.05	200.0
		0	0.143	0.401	0.145	2×10^{-3}	2×10^{-5}
$x=0.1$		-1	-1.000	-0.963	-0.482	-0.060	-0.006
		1	0.998	0.884	0.871	0.998	1.000
		1.2	1.201	1.246	2.492	20.1	200.0
		0	2×10^{-3}	0.116	0.129	2×10^{-3}	2×10^{-5}
$x=1$		-1	-1.000	-0.998	-0.822	-0.148	-0.015
		1	1.000	0.999	0.974	0.998	1.000
		3	3.000	3.007	3.650	20.2	200.0
		0	6×10^{-6}	6×10^{-4}	0.026	2×10^{-3}	2×10^{-5}
$x=10$		-1	-1.000	-1.000	-0.995	-0.724	-0.104
		1	1.000	1.000	1.000	0.999	1.000
		21	21.0	21.0	21.1	29.0	201.1
		0	2×10^{-9}	2×10^{-7}	2×10^{-5}	6×10^{-4}	2×10^{-5}
$x=100$		-1	-1.000	-1.000	-0.999	-0.995	-0.709
		1	1.000	1.000	1.000	1.000	1.000
		201	201.0	201.0	201.0	202.0	283.6
		0	2×10^{-13}	2×10^{-11}	2×10^{-9}	2×10^{-7}	6×10^{-6}

[a] In each entry the upper number is either ν_α or ν_β, the lower number is the corresponding f_α or f_β. See text for definition of x, y, z, and ν.

in that case $f_\alpha \approx 1$, $\omega_\alpha \approx \omega_a$.

(iv) A second case of (ii) appears when

$$2V \gg \hbar|\omega_b - \omega_a| \text{ and } E_b - E_a < 2V;$$

in this case $f_\alpha \approx 1$, $\omega_\alpha \approx \frac{1}{2}(\omega_a + \omega_b)$.

(v) In the absence of hybridization, $V=0$, only the ω_a frequency is observed: $f_\alpha = 1$; $\omega_\alpha = \omega_a$.

(vi) Two different frequencies of comparable oscillator strength are observed only if

$$E_b - E_a < \hbar|\omega_b - \omega_a| \text{ and } 2V < \hbar|\omega_b - \omega_a|.$$

These are necessary but not sufficient conditions.

(vii) If conditions (vi) are satisfied and

$$E_b - E_a < 2V,$$

then the two frequencies have comparable strengths $f_\alpha \gtrsim f_\beta$.

(viii) If conditions (vi) are satisfied, but

$$E_b - E_a > 2V \text{ and } \omega_b > \omega_a,$$

then $\omega_\alpha \approx \omega_a$ and $f_\alpha \approx 1$, i.e., a pure "unhybridized" state dominates.

(ix) If $\omega_b < \omega_a$, $2V < \hbar|\omega_b - \omega_a|$ and $E_b - E_a \approx \hbar(\omega_a - \omega_b)$, then both frequencies are very similar $\omega_\alpha \approx \omega_\beta \approx \omega_a$ and have comparable oscillator strengths

$$f_\alpha \gtrsim f_\beta.$$

(x) Finally if $\omega_b < \omega_a$ and $E_b - E_a = \frac{1}{2}\hbar(\omega_a - \omega_b)$ a special case appears: The lower-frequency ω_α is always equal to the average frequency

$$\omega_\alpha = \frac{1}{2}(\omega_a + \omega_b),$$

but its strength varies from $f_\alpha \approx 0$ for small V to $f_\alpha \approx 1$ for very large V.

From the above observations it can be seen that

TABLE II. Frequencies ν and oscillator strengths f for $z=-1$ $(\omega_b < \omega_a)$. [a]

	$y=0$	$y=0.01$	$y=0.1$	$y=1$	$y=10$	$y=100$
$x=0$	-1	-0.990	-0.905	-0.414	-0.050	-0.005
	?	0.505	0.550	0.854	0.998	1.000
	1	1.010	1.105	2.414	20.05	200.0
	?	0.495	0.450	0.146	2×10^{-3}	2×10^{-5}
$x=0.01$	-0.98	-0.976	-0.895	-0.407	-0.050	-0.005
	0	0.150	0.500	0.852	0.998	1.000
	1	1.004	1.096	2.407	20.05	200.0
	1	0.850	0.500	0.148	2×10^{-3}	2×10^{-5}
$x=0.1$	-0.8	-0.800	-0.764	-0.340	-0.040	-0.004
	0	3×10^{-3}	0.188	0.837	0.998	1.000
	1	1.001	1.047	2.350	20.04	200.0
	1	0.997	0.812	0.163	2×10^{-3}	2×10^{-5}
$x=0.5$	0	0	0	0	0	0
	0	4×10^{-4}	0.038	0.800	0.998	1.000
	1	1.000	1.020	2.236	20.02	200.0
	1	1.000	0.962	0.200	2×10^{-3}	2×10^{-5}
$x=1$	1	0.990	0.905	0.414	0.050	0.005
	p	0.505	0.550	0.854	0.998	1.000
	1	1.010	1.105	2.414	20.05	200.0
	$(1-p)$	0.495	0.450	0.146	2×10^{-3}	2×10^{-5}
$x=10$	1	1.000	1.000	0.994	0.687	0.095
	1	1.000	1.000	1.000	0.999	1.000
	19	19.000	19.00	19.11	27.60	200.9
	0	3×10^{-9}	3×10^{-7}	3×10^{-5}	7×10^{-4}	2×10^{-5}
$x=100$	1	1.000	1.000	1.000	0.995	0.705
	1	1.000	1.000	1.000	0.100	1.000
	199	199.0	199.0	199.0	200.0	282.1
	0	2×10^{-13}	3×10^{-11}	3×10^{-9}	2.5×10^{-7}	6×10^{-6}

[a] In each entry the upper number is either ν_α or ν_β, the lower number is the corresponding f_α or f_β. See text for definition of x, y, z, and ν.

the signals obtained by the outside coupling of a measuring system (harmonic oscillator) to a hybridized system cannot be naively interpreted without detailed analysis.

In the "adiabatic" or "static" limits in which $\hbar | \omega_a - \omega_b |$ is much smaller than either V or $b_b - b_a$, only one frequency is observed. This frequency is the averaged value, with proper weights, of ω_a and ω_b. This limit corresponds to measurements of, for example, lattice constants[3] and isomer shifts.[9] In this last case since the measuring energies involved ($\sim 10^{-6}$ eV) are several orders of magnitude smaller than the configuration energy difference or the hybridization matrix

element (both approximately $10^{-1}, 10^{-2}$eV) only one line is observed.

In the "sudden" or high-frequency approximation when $\hbar | \omega_b - \omega_a |$ is of the order of or larger than both the energy difference and the hybridization energy, it is possible to observe two distinct signals of comparable strength—this happens only when condition (vi) is satisfied. Such is the case in the photoemission experiments[7] in which the energy separation between responses of the configurations (5–10 eV) is several orders of magnitude larger than both the configuration energy difference and the hybridization energy.

We would like to point out that our treatment,

through the use of the time-energy uncertainty relation, can be qualitatively cast into a language of "measuring time" $|\omega_b - \omega_a|^{-1}$ versus "fluctuation times," either $\hbar/V$ or $\hbar/(E_b - E_a)$, and a comparison between them. Such an approach is, however, misleading since we are concerned here with ground-state properties which are, by necessity, stationary.

In conclusion we would like to point that the region in which $\hbar|\omega_b - \omega_a|$, V, and $E_b - E_a$ are all comparable exhibits the most complicated and interesting behaviors. It would be therefore of great interest to explore the mixed-valence solids with probes whose typical energy is in the 0.01–0.1 eV region, where such behaviors are bound to occur.

[1]K. A. Gschneidner and R. Smoluchowski, J. Less-Common Met. 5, 374 (1963).

[2]A. Jayaraman, V. Narayanamurti, E. Bucher, and R. G. Maines, Phys. Rev. Lett. 25, 1430 (1970).

[3]A. Jayaraman, P. Dernier, and L. D. Longinotti, Phys. Rev. B 11, 2783 (1975).

[4]C. E. T. Gonçalves da Silva and L. M. Falicov, Solid State Commun. 17, 1521 (1975).

[5]M. Avignon and S. K. Ghatak, Solid State Commun. 16, 1243 (1975).

[6]M. B. Maple and D. Wohlleben, Phys. Rev. Lett. 27, 511 (1971).

[7]M. Campagna, E. Bucher, G. K. Wertheim, D. N. E. Buchanan, and L. D. Longinotti, Phys. Rev. Lett. 32, 885 (1974).

[8]B. B. Triplett, N. S. Dixon, P. Boolchand, S. S. Hanna, G. Langouche, and E. Bucher (private communication and unpublished).

[9]E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, Phys. Rev. Lett. 30, 1053 (1973).

[10]T. Penney and F. Holtzberg, Phys. Rev. Lett. 34, 322 (1975).