PHYSICAL REVIEW A VOLUME 20, NUMBER 5 NOVEMBER 1979

Perturbed Rydberg series: Relationship between quantum-defect and configuration-interaction theory

F. H. Mies

Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234

(Received 15 November 1978; revised manuscript received 24 May 1979)

In this paper the theory of a single Rydberg series perturbed by an interloping state is examined. General analytic expressions are presented which apply both to the bound-state regions and to the autoionizing regions above the Rydberg ionization limit. The parameters are expressed in terms of configuration-interaction matrix elements, which can be calculated *a priori*. There is no restriction to weak-perturbation theory, and the wave function and all its associated properties, such as transition moments, can be extracted. Explicit calculations are presented for the Cd$(5s\ nd)\,^1D_2$ series perturbed by the Cd$(5p^2)\,^1D_2$ valence state, and excellent results are obtained.

I. INTRODUCTION

The theoretical calculation of atomic and molecular wave functions by variational techniques, which utilize trial functions to describe the individual electron orbitals, has worked very well for the lowest-energy states of a given symmetry. This is particularly true for "valence states," i.e., states whose predominant configurations are constructed from valence orbitals. In principle, the methods can be used to obtain excited states of the same symmetry by promoting the electrons to Rydberg-type orbitals. However, at these higher energies other configurations become almost degenerate, and the calculations must be expanded to include multi-configuration interactions. In particular, the interaction between a Rydberg state and an *excited* valence configuration can be quite strong, and the entire concept of a valence state and Rydberg state becomes confused. The problem of maintaining orthogonality between succeeding eigenstates also becomes a chore, and no simple methods have been devised to extrapolate the results to high principal quantum numbers.

Our goal in this paper is to demonstrate that there is a wealth of information about excited electronic states buried in present day *ab initio* calculations that can be extracted simply be recognizing the analytic properties of Rydberg states. This can be accomplished by incorporating multi-channel quantum defect theory (QDT). into the framework of configuration interaction and variational theories for bound electronic states. The results of QDT are derived by utilizing the analytic properties of the Rydberg electron for *arbitrary* energy. However, we will show that the necessary parameters can be obtained from *ab initio* calculations at *discrete* energies, without any modification of the codes that are presently employed. The QDT, with parameters derived from low-energy variational calculations, allows us to describe the properties of electronic states at higher energies, including the continuum. This is particularly imperative for molecular Rydberg series, where experimental data are both imprecise and difficult to interpret.

The theory is developed for the simplest conceivable case of a single Rydberg series, originating from an $L=0$ ion core, that is perturbed by a single interloping state originating from a different configuration. There is no restriction on the strength of the perturbation, and the perturbing level may lie imbedded within the series, or equally well, lie within the ionization continuum, in which case autoionization is encountered.

The theory is applied to an analysis of *ab initio* calculations for the Cd $(^1D_2)$ Rydberg series which converges to the Cd$^+$ $(^2S_{\frac{1}{2}})$ ground-state ion. The experimental term values are shown in Fig. 1, and are measured in units of $e^2/2a_0$ with respect to the ionization limit where $\epsilon=0$. This system was very carefully chosen for its simplicity and conformity to the present theoretical model. The unperturbed series originates from the Cd $(5s\ nd)$ $^1D_2$ configuration. The unperturbed levels, $n=5-10$, calculated by Stevens[1] are shown in Fig. 1. In addition, a Cd $(5p^2)$ $^1D_2$ valence state calculated to exist at E_p, approximately 1 eV *above* the ionization limit, strongly interacts with the series. Aside from higher members of the Cd $(5p\,np)$ $^1D_2$ series, which can be incorporated into the theory with little modification, no other significant perturbations are expected.

In Sec. II we review the quantum-defect theory[2] for a single unperturbed series. The asymptotic behavior of the Rydberg orbital is expressed as an analytic function of the continuous energy variable,

$$\epsilon=-1/\nu^2\,. \tag{1}$$

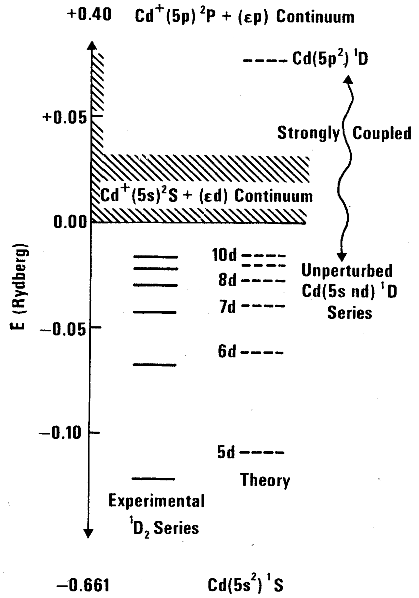

FIG. 1. Energy levels (Ry) of Cd $^1D_2$ series relative to the Cd$^+$ (5s) $^2S_{1/2}$ ionization limit. The theoretical levels for the unperturbed Cd (5s nd) $^1D_2$ series and the perturbing Cd (5p^2) $^1D_2$ valence state were calculated by Stevens (Ref. 1). The matrix elements for these strongly coupled states are given in Table I.

At large distances, the orbital radial function must be a solution of the second-order Coulomb equation and can be uniquely represented as a linear combination of the regular and irregular Coulomb functions in terms of a single parameter $\tan\xi^0$. For arbitrary $\epsilon<0$ the Coulomb functions contain exponentially rising terms and the solution is not well behaved. The eigenvalues ϵ_n^0 are determined by the following condition which insures that the amplitude which multiplies these terms vanishes and the resultant orbital exponentially decays at large distances,

$$\tan\pi(\nu+\mu^0)=0\,. \qquad (2)$$

This equation imposes the requirement that $\nu=n-\mu^0$, for integer values of $n\geqslant l+1$ and yields the usual expression for the Rydberg eigenvalues,

$$\epsilon_n^0=-1/(n-\mu^0)^2\,. \qquad (3)$$

The defect, $\mu^0=\mu^0(\epsilon)$, is a slowly varying function of ϵ

$$\tan\pi\mu^0=A(\epsilon)/[\cot\pi\xi^0+\mathcal{G}(\epsilon)]\underset{\epsilon\to 0}{\sim}\tan\pi\xi^0\,. \qquad (4)$$

A and $\mathcal{G}$ are monotonic functions of ϵ which approach 1 and 0, respectively, at the ionization limit and are known functions[2] defined by the orbital angular momentum l of the Rydberg orbital. The Rydberg series is uniquely defined by the parameter $\xi^0=\xi^0(\epsilon)$ which is a slowly varying analytic function of ϵ. The slowly varying nature of $\mu^0(\epsilon)$ and $\xi^0(\epsilon)$ is, of course, the essence of the QDT. The parameters may be determined from an analysis of the *ab initio* calculations for the unperturbed series.

In Sec. III the theory is developed for the perturbation of the series caused by a single interloping state. A very simple analytic representation of the perturbation of the eigenvalues is obtained, in which the quantum defect μ^0 in Eqs. (2) and (3) is replaced by μ_p,

$$\tan\pi\mu_p=A/[\cot\pi(\xi^0+\lambda_P)+\mathcal{G}]\underset{\epsilon\to 0}{\sim}\tan\pi(\xi^0+\lambda_P)\,. \qquad (5)$$

The perturbation introduces an "energy-dependent" phase shift λ_p given by

$$\tan\pi\lambda_P=-\Gamma/2(\epsilon-\overline{E}_P) \qquad (6)$$

which is added to the phase shift ξ^0 for the unperturbed series. $\overline{E}_P$ is the "position" of the perturbing level, possibly modified by a principal part "shift" which we shall ignore for present purposes. The "width" $\Gamma=\pi V_p^2$ is a measure of the strength of the interaction.

In Sec. IV we determine the normalization of the perturbed wave function and show how Γ can be evaluated from the usual configuration-interaction (CI) matrix elements between the perturbed and the unperturbed Rydberg states. Even without recourse to theoretical calculations, Eq. (5) is a very useful representation for analyzing a perturbed series. The parameter $\pi\lambda_P(\epsilon)$ introduced by the perturbing level varies from zero, as $\epsilon\to-\infty$, to $\frac{1}{2}\pi$ at $\epsilon=\overline{E}_P$, to π as $\epsilon\to+\infty$. The energy dependence of the unperturbed parameter ξ_0 is modified in such a way as to introduce an *additional* eigenvalue into the spectrum of the Rydberg levels. If the width $\Gamma=\pi V_P^2$ is very small, then the additional level will be well localized in analogy to the usual perturbation results. However, a large width will spread the contribution of the perturbing state over the entire Rydberg series and possibly into the ionization continuum, where it can influence the photoionization spectrum.

In Sec. V the theory is applied to the Cd ($^1D_2$) series. Conclusions are summarized in Sec. VI.

II. THEORY OF UNPERTURBED RYDBERG SERIES

We shall assume LS coupling is valid for the given, *unperturbed* Rydberg series. Further, we only consider the simplest case of a series originating from an *ion*-core state $|L_c,M_{L_c};S_c,M_{S_c}\rangle=\phi_0(\vec{r}_c)$ with total orbital angular momentum $L_c=0$. This may be combined with the spin functions, $|s,m_s\rangle$, of the $s=\frac{1}{2}$ Rydberg electron to define a total spin $\vec{S}=\vec{S}_c+\vec{s}$, which is *assumed* to commute with the total Hamiltonian $H_T(\vec{r}_c,\vec{r})$.

$$|S,M_S\rangle = \sum_{M_{S_c},\, m_s} \phi_0(\vec{r}_c)\,|s,m_s\rangle \times C(S_c,s,S;M_{S_c},m_s,M_S)\ . \qquad (7)$$

The Rydberg orbital, $\psi_0(\vec{r}) = Y_{l,m_l}(\hat{r})\rho_0(r)/r$, with orbital angular momentum l defined by the Legendre function $Y_{l,m_l}(\hat{r})$, is described by a radial function $\rho_0(r)$ which must be well behaved at the origin, i.e.,

$$\rho_0(r) \underset{r\to 0}{\sim} (2r)^{l+1}/(2l+1)\,! \qquad (8)$$

We shall be particularly concerned about the long-range properties of $\rho_0(r)$.

The general function for the Rydberg state can be expressed as an antisymmetrized product,

$$|\alpha_0;\rho_0\rangle = \mathfrak{A}[\,|S,M_S\rangle\psi_0(\vec{r})] = \mathfrak{A}\,[\,|\alpha_0\rangle\rho_0(r)/r]\,, \qquad (9\text{a})$$

where

$$|\alpha_0\rangle \equiv |S,M_S;l,m_l\rangle = |S,M_S\rangle Y_{l,m_l}(\hat{r}) \qquad (9\text{b})$$

and the antisymmetrization operator $\mathfrak{A}$ is normalized such that

$$\langle\alpha_0,\rho_0\,|\,\alpha_0,\rho_0'\rangle = \int_0^\infty dr\,\rho_0^*(r)\rho_0'(r)\ . \qquad (9\text{c})$$

We can construct a complete set of states $\{\alpha\}$ from the complete set of ion-core states, $\{\phi_c(\vec{r}_c)\} = \{\phi_0,\phi_1 \ldots\}$, and the various orbital angular momentum states $Y_{l,m_l}(\hat{r})$. These are referred to as channel states, and they play an important role in QDT and scattering theory. The channel states are simple product functions which already contain the orbital and spin angular momentum of the Rydberg electron. They span the entire space of the system, *with the exclusion of the Rydberg radial coordinate r*. The total wave function $|E\rangle$, at total energy E, is expanded in a truncated set of channel states

$$|E\rangle = \sum_i C_i\,|\alpha_i;\rho_i\rangle\,, \qquad (10)$$

and coupled integro-differential equations are generated for the radial functions $C_i\rho_i(E,r)/r$,

$$\langle\alpha_i\,|H_T(\vec{r}_c,\vec{r}) - E\,|E\rangle = 0 \ \text{ for all } i\,. \qquad (11)$$

In the limit of large r, where the Rydberg electron is ionized and its interaction with the core electrons vanishes, these channel states $|\alpha\rangle$ *must be uncoupled* by the total Hamiltonian $H_T(\vec{r}_c,\vec{r})$. (This is the *definition* of a channel state. The assumption concerning LS-coupling for the ion-core states can be removed by selecting appropriate combinations of "approximate" channel states which properly diagonalize the *asymptotic* spin-orbit interaction.) The asymptotic Hamiltonian is separable and the channel states define the following differential equation for the radial portion of the total wave function:

$$\langle\alpha_i\,|H_T - E\,|E\rangle \underset{r\to\infty}{\sim} C_i\left((E_{\alpha_i} - E) - \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{l_i(l_i+1)}{r^2} - \frac{2}{r}\right)\frac{\rho_i(E,r)}{r} = 0 \qquad (12\text{a})$$

This is, of course, the Coulomb equation. *Each* α *state defines an ionization limit*, with the threshold energy E_α and an orbital angular momentum l for the escaping electron. Therefore, *each* $|\alpha\rangle$ *identifies an entire unperturbed Rydberg series.* QDT examines the analytic properties of the radial functions in each channel. Whenever E equals a proper bound-state eigenvalue E_n, the radial functions must vanish asymptotically,

$$\sum_i C_i\,\frac{\rho_i(E,r)}{r} \underset{r\to\infty}{\sim} 0\,, \quad E = E_n\,. \qquad (12\text{b})$$

For the one-channel expansion $|E\rangle = C_0\,|\alpha_0;\rho_0\rangle$ defined in Eq. (9), ρ_0 must satisfy Eqs. (11) and (12) for $E_{\alpha_i} = E_{\alpha_0}$.

Seaton[2] has defined Coulomb functions $f(\epsilon,r)$ and $g(\epsilon,r)$ that are solutions of the Coulomb equation (12a) and are *analytic* functions of the asymptotic energy ϵ,

$$\epsilon = (E - E_\alpha)\ . \qquad (13)$$

Further, these functions are exact, independent solutions of Eq. (12a) for *all* ϵ and *all* r, with the Wronskian normalized as follows,

$$f\frac{\partial g}{\partial r} - g\frac{\partial f}{\partial r} = \frac{2}{\pi}\ . \qquad (14)$$

The leading terms in the power-series expansion of f and g are independent of ϵ; in fact, Eq. (8) is equivalent to the expansion of the solution f, which is regular as $r\to 0$, while g approaches $-(2l)\,!/\pi(2r)^l$ and is divergent at the origin. The radial function $\rho_0(\epsilon,r)$ is related to these functions as follows:

$$\begin{aligned} &\rho_0 \underset{r\to 0}{\sim} f(\epsilon,r) \\ &\rho_0 \equiv \psi_R^0(\epsilon,r)\mathfrak{C} \end{aligned} \qquad (15)$$

where

$$\psi_R^0 \underset{r\to\infty}{\sim} (f\cos\pi\xi^0 - g\sin\pi\xi^0)\ . \qquad (16)$$

The important parameter $\xi^0 = \xi^0(\epsilon)$ is a slowly varying analytic function of ϵ. The single-channel expansion $|E\rangle = C_0\,|\alpha_0;\rho_0\rangle$ defines a solution of Eq. (11) which is exact and has its asymptotic properties given by Eq. (16) for *all E*. However, for $E < E_{\alpha_0}$, well-behaved solutions, which are square integrable, are only obtained at *particular* eigenvalues $E = E_n^0 = \epsilon_n^0 + E_{\alpha_0}$, when ψ_R^0 vanishes asymptotically, i.e.,

$$\psi_R^0(\epsilon_n^0, r) \underset{r\to\infty}{\sim} 0 . \tag{17}$$

The asymptotic properties of f and g have been well described by Seaton, and, for $\epsilon < 0$, both functions contain exponentially rising functions Φ^-. The discrete eigenvalues defined by (17) occur when the amplitude associated with the Φ^- components in Eq. (16) vanishes. Seaton has shown this condition is satisfied when

$$[\cos\pi\xi^0 + \sin\pi\xi^0(\mathcal{G} + A\cot\pi\nu_n^0)]\frac{\Phi^-}{\Gamma(l+1-\nu_n^0)} = 0 , \tag{18}$$

where

$$\epsilon_n^0 = -1/(\nu_n^0)^2 . \tag{19}$$

Except for $\xi^0 = 0$ [which corresponds to the "pure" Coulomb case, where the eigenvalues occur at the poles of the γ function $\Gamma(l+1-\nu_n^0)$, i.e., $\nu_n^0 = l+1, l+2, \ldots$] the eigenvalues are defined by the condition

$$\cot\pi\xi^0 + \mathcal{G} + A\cot\pi\nu_n^0 = 0 . \tag{20}$$

Letting

$$\cot\pi\mu^0 = (\mathcal{G} + \cot\pi\xi^0)/A , \tag{21}$$

we obtain Eqs. (1)–(4) in which the eigenvalues occur at $\nu_n^0 = (n - \mu^0)$, with $n = l+1, l+2, \ldots$, such that

$$E_n^0 = E_{\alpha_0} - 1/(n-\mu^0)^2 . \tag{22}$$

$\mu^0(\epsilon_n^0)$ is the "quantum defect" for the state with eigenvalues E_n^0 and is related to the parameter ξ^0 through Eq. (21). The parameter A is a function of ϵ and l

$$A = \prod_{p=0}^{l}(1 + p^2\epsilon) \tag{23}$$

and, $A \to 1$, as $\epsilon \to 0$. The function $\mathcal{G}$ is not analytic in ϵ and is given in terms of the Ψ functions,[3] which are logarithmic derivatives of Γ functions,

$$\mathcal{G}(\nu, l) = \frac{A}{2\pi}[\psi(\nu + l + 1) + \psi(\nu - l) - 2\ln\nu] . \tag{24}$$

This function approaches zero as $\epsilon \to 0$. Only at threshold, $\epsilon = 0$, does $\mu^0 = \xi^0$. The *known* functions A and $\mathcal{G}$ introduce significant energy variation in the quantum defect μ^0, especially for $l \neq 0$; generally much more substantial extrapolation of the spectra can be obtained from an analysis based on ξ^0 held constant, with μ^0 varying according to Eq. (21).

The usual self-consistent-field (SCF) variational calculations construct a trial function similar to Eqs. (7) and (9), but with one important exception. The ion-core function $\phi_0(\vec{r}_c)$ in QDT is constrained to be the asymptotic ion-core state of the ionized system. The only variable in the wave function is the radial function $\rho_0(r)$ [*and* the number of ion-core channels included in the expansion of Eq. (10)]. SCF calculations, on the other hand, replace $\phi_0(\vec{r}_c)$ by a variational trial function ϕ_0^v which is not necessarily an eigenfunction of the ion-core Hamiltonian, and *both* ϕ_0^v and ρ_0^v are varied to obtain a best energy.

If we use the single configuration $|\alpha_0^v;\rho_0^v\rangle$ in a variational calculation, we will obtain a set of eigenvalues E_n^v, which represent the Rydberg levels of the *unperturbed* series originating from the $L_c = 0$ core and an l Rydberg electron. For an $l = 2$ electron, which corresponds to, say, the $\ldots 5s\,(^2S_{1/2})\; nd\,^1D$ series of Cd, we might expect that the variationally calculated core function will closely approximate the true ion-core state. Certainly as n becomes large and the Rydberg electron density within the core diminishes (as n^{-3}), this will be true. For present purposes we will *assume* $\phi_0^v \equiv \phi_0$ and the radial function $\rho_0(r)$ is the only variational function. In this case, with no core polarization, both variational theory and QDT give identical results, i.e., $E_n^v = E_n^0$ in Eq. (22). Let

$$|E_n^0\rangle = N_n^0 |\alpha_0;\rho_0(E_n^0)\rangle , \tag{25}$$

where ρ_0 is the variationally determined radial wave function with boundary conditions given by Eq. (8) in the frozen field of the $^2S_{1/2}$ core. Let

$$F_n^0(r) = N_n^0\rho_0(E_n^0, r) \equiv (N_n^0\mathcal{C})\psi_R^0(E_n^0, r) \tag{26}$$

such that

$$\int F_n^{0*}(r)F_{n'}^0(r)\,dr = \delta_{n,n'} \tag{27}$$

and

$$\langle E_n^0|H_T|E_{n'}^0\rangle = E_n^0\delta_{n,n'} . \tag{28}$$

Given a set of eigenvalues $\{E_n^0\}$ determined from the variational solution of Eq. (11), we obtain a "quantum defect" $\mu^0(E_n^0)$ from Eq. (22) and then use Eq. (21) to determine the parameter $\xi^0(E_n^0)$. *If* the amplitudes of the functions f and g in Eqs. (15) and (16) are determined primarily in the range of small r values where $f(\epsilon, r)$ and $g(\epsilon, r)$ are almost independent of ϵ, then we might expect $\xi^0(\epsilon)$ to be only a slowly varying function of ϵ. This requires that all interactions, except the asymptotic Coulomb and centrifugal terms in Eq. (12a) vanish rapidly with increasing r. The QDT is predicated on this fact that ξ^0 is an insensitive function of ϵ, particularly in the vicinity of the threshold. Calculated ξ^0 values of the Cd ($5s\ nd$) $^1D_2$ Rydberg series are given in Table I and exhi-

TABLE I. Calculated properties of CdI $(5s\ nd)^1D_2$.

Term	Unperturbed eigenvalues E_n^0 (Ry) (calculated)	(μ^0-2) (derived)	(ξ^0-2) (derived)	CI matrix element $\langle P\,\vert\, H_T\,\vert\, E_n^0\rangle$	Γ(Ry) (derived)
$5s5d$	−0.108 504 9	−0.035 815	−0.071 404	−0.044 414	0.298 56
$5s6d$	−0.061 173 5	−0.043 135	−0.061 068	+0.027 650	0.224 23
$5s7d$	−0.039 266 6	−0.046 477	−0.057 541 [a]	−0.020 014	0.199 99 [a]
$5s8d$	−0.027 319 9	−0.050 075	−0.057 902	+0.015 557 2	0.194 52
$5s9d$	−0.020 084 4	−0.056 198	−0.062 444	−0.012 951 2	0.205 48
$5s10d$	−0.015 364 0	−0.067 663	−0.073 274	+0.010 899	0.211 81
$(5p)^2$	+0.076 938 5 [a]				

[a] Optimum parameters chosen: $(\xi^0-2)=-0.057\,541$; $\Gamma=0.199\,99$ Ry, $\bar{E}_p=0.076\,938\,5$ Ry.

bit this desired feature.

Note that by using the nondivergent SCF solutions $|E_n^0\rangle$, we have obtained an asymptotic analytic representation of the radial function $\psi_R^0(\epsilon,r)$ for *all* energies. This function is regular at the origin and, for $\epsilon>0$, is just the scattering, or continuum, wave function, in channel α_0. The asymptotic form of ψ_R^0 yields a scattering phase shift δ_0 in terms of the parameter ξ^0, i.e.,[4]

$$\psi_R^0(\epsilon,r)\underset{\substack{r\to\infty\\ \epsilon>0}}{\sim}\left(\frac{2\gamma}{\pi}\right)^{1/2}B^{1/2}\frac{\sin\pi\xi^0}{\sin\pi\delta^0}\sin(\omega+\delta^0)\,, \qquad (29)$$

where the phase shift is given by

$$\cot\delta_0=[\cot\pi\xi^0+R_e(\mathcal{G})]/B\,,$$

where $\gamma^2=1/\epsilon$, $R_e(\mathcal{G})\equiv\frac{1}{2}(\mathcal{G}+\mathcal{G}^*)$, $B=A(\epsilon,l)/[1-\exp(-2\pi\gamma)]$ and

$$\omega=r/\gamma+\gamma\ln(2r/\gamma)-\tfrac{1}{2}\pi l-\arg(\Gamma(l+1+i\gamma))\,.$$

Near threshold, where $\gamma\to\infty$, $\epsilon\to0^+$, $B\approx A\approx1$, and $R_e(\mathcal{G})\approx0$, we obtain

$$\delta^0\approx\pi\mu^0\approx\pi\xi^0\quad\text{as }\epsilon\to0^+\,. \qquad (30)$$

In addition to the function $\psi_R^0(\epsilon,r)$, which is regular at the origin, we can obtain an *independent* solution at energy ϵ, which is also analytic in ϵ and irregular at the origin. We define $\psi_I^0(\epsilon,r)$ by the following Wronskian condition,

$$\psi_R^0\frac{\partial\psi_I^0}{\partial r}-\psi_I^0\frac{\partial\psi_R^0}{\partial r}=2/\pi\,, \qquad (31)$$

where $\psi^0_I\underset{r\to0}{\sim}g(\epsilon,r)\mathcal{C}$ and

$$\psi_I^0\underset{r\to\infty}{\sim}(f\sin\pi\xi^0+g\cos\pi\xi^0) \qquad (32)$$

Both ψ_R^0 and ψ_I^0 are solutions of the equation

$$\langle\alpha_0|H_T-(E_{\alpha_0}+\epsilon)|\alpha_0,\ \psi^0(\epsilon)\rangle=0\,. \qquad (33)$$

It should be recognized that, for $\epsilon>0$, the solution $\psi_R^0(\epsilon,r)$ corresponds to the distorted-wave approximation (DWA)[5] in channel $|\alpha_0\rangle$ in the absence of coupling to other channels.

III. PERTURBATION OF THE RYDBERG SERIES

Let us suppose that, in addition to the ground-state series $|E_n^0\rangle$ in Eq. (25), we have determined various, *excited*, variational channel state wave functions which have the following properties.

$$|P\rangle=\sum_{i\neq0}C_i^P|\alpha_i{:}\rho_i^P\rangle \qquad (34\text{a})$$

such that

$$\langle P|H_T|P'\rangle=E_P\delta_{P,P'} \qquad (34\text{b})$$

with the additional condition that the following integral vanish for *any* arbitrary radial function $F(R)$,

$$\langle P|\alpha_0;F\rangle=0\,. \qquad (35)$$

The "perturbing" states $|P\rangle$ correspond to *well-behaved* bound-state solutions originating from *excited* ion-core states $|\alpha_i\rangle$ and are orthogonal to the unperturbed Rydberg series with $F=F_n^0$ given by Eq. (26). This will generally be true, especially if the set of channel states $|\alpha_i\rangle$ only contain core angular momenta L_c and Rydberg orbital angular momenta l which both differ from the values in $|\alpha_0\rangle$ [see Eqs. (7) and (9)]. If $|P\rangle$ is generated from a variational calculation which allows arbitrary variations in the core functions, then small nonorthogonalities *may* be introduced which invalidate Eq. (35), but only in very special cases, generally involving configurations with excited cores of the same symmetry as $|\alpha_0\rangle$. These complications are not present in the Cd$(^1D_2)$ calculations, and can be treated, if necessary, with minor variation of the present theory. We shall proceed with the assumption contained in Eq. (35).

If we consider just one perturbing state, and one Rydberg series, we obtain a particularly simple result. Let

$$|E\rangle = |\alpha_0;F_E\rangle + B_P(E)\,|P\rangle\,, \tag{36}$$

where we must choose the coefficient $B_P(E)$, and the radial function $F_E(r)$ to satisfy the condition

$$\langle E'|H_T - E|E\rangle = 0 \tag{37}$$

for *all* E and E' and such that $|E\rangle$ is well behaved.

Equation (36) may be regarded as a restricted version of the multichannel QDT expressed in Eqs. (10)–(12). The excited channel states, with $\alpha_i \neq \alpha_0$, have been collected together in Eq. (34a), and by some variational technique the radial functions $C_i^P \rho_i^P$ have been generated which decay asymptotically and satisfy Eq. (12b) when $E = E_P$. This set is "frozen" and introduced into Eq. (36) with one linear parameter $B_P(E)$ which must be adjusted to satisfy Eq. (37). Ideally the QDT would allow each $C_i \rho_i$ function to vary independently until Eqs. (11) and (12) are satisfied, and in this sense Eq. (36) is much more restrictive. However, since the variationally determined state $|P\rangle$ can indirectly encompass the *infinite* set of channel states, it offers compensations that are not easy to assess.

From another point of view, Eq. (36) is exactly equivalent to Fano's configuration interaction theory[6] (CIT) for a single resonance imbedded in a continuum. Fano simply expands the undetermined function F_E using the *complete* set of *well-behaved* solutions for the unperturbed series that were generated in Sec. II,

$$F_E^{\mathrm{CIT}}(r) = \sum_n A_n(E) F_n^0(r) + \int_0^\infty d\epsilon'\, C_{\epsilon'}(E)\, \psi_R^0(\epsilon', r)\,, \tag{38}$$

where F_n^0 is defined in Eq. (26) for the bound eigenstates and ψ_R^0 has the asymptotic properties in Eqs. (16) and (29) for $E' = E_{\alpha_0} + \epsilon'$ above the ionization limit. $F_E^{\mathrm{CIT}}(r)$ vanishes at the origin, and is always nondivergent for $r \to \infty$. The coefficients $A(E)$ and $C(E)$ are determined from Eq. (37). Below the ionization limit $E < E_{\alpha_0}$, solutions are obtained *only* at discrete energies $E = E_n$ which define the eigenvalues for the perturbed series.

In contrast, we shall expand $F_E(r)$ as follows:

$$F_E(r) = \psi_R^0(\epsilon, r) - \tan\pi\lambda_P G_I(\epsilon, r)\,, \tag{39a}$$

where G_I is required to be well behaved as $r \to 0$, and asymptotically

$$G_I(\epsilon, r) \underset{r\to\infty}{\sim} \psi_I^0(\epsilon, r)\,. \tag{39b}$$

Note that ψ_R^0 and F_E are not yet normalized. Also, the entire perturbed radial dependence has been incorporated into the function G_I. When the parameter $\lambda_P = 0$, for all ϵ, we retrieve the unperturbed solution ψ_R^0. Unlike F_E^{CIT} in Eq. (38) which is well behaved and only defines solutions at discrete energies E_n when E is below the ionization limit, F_E in Eq. (39) yields mathematically proper solutions at *all* energies using the unperturbed radial functions $\psi_R^0(\epsilon, r)$ and $\psi_I^0(\epsilon, r)$ *on* the energy shell $E = E_{\alpha_0} + \epsilon$. Of course these functions are asymptotically divergent when $\epsilon < 0$ and well-behaved solutions must be extracted, in analogy to Eq. (17), by imposing the condition $F_E(r) \sim 0$ as $r \to \infty$.

Let us define the following matrix elements:

$$V_P \equiv \langle P|H_T - E|\alpha_0;\psi_R^0(\epsilon)\rangle\,, \tag{40}$$

$$W_P \equiv \langle P|H_T - E|\alpha_0;G_I(\epsilon)\rangle\,, \tag{41}$$

and a shifted energy for the perturbing state $|P\rangle$,

$$\overline{E}_P = E_P + \tfrac{1}{2}\pi W_P V_P\,. \tag{42}$$

The term $\frac{1}{2}\pi W_P V_P$ in Eq. (42) corresponds to the principal-part shift one obtains in CIT.[6] Since we have no simple method of evaluating W_P with any certainty, we shall introduce it as the sole adjustable parameter in the present theory. (It is possible that multi-configuration calculations can be used to estimate the shift $\frac{1}{2}\pi W_P V_P$, or explicit numerical integrations can be employed using pseudopotential methods.) The Cd results are obtained *assuming* $\overline{E}_P = E_P$.

From Eqs. (36), (37), and (39) we obtain the algebraic equation

$$\langle P|H_T - E|E\rangle = B_P(E)(E_P - E) + V_P - \tan\pi\lambda_P W_P = 0 \tag{43}$$

and an integro-differential equation for the radial function $F_E(r)$,

$$\langle \alpha_0|H_T - E|\alpha_0;F_E\rangle + B_P(E)\langle \alpha_0|H_T - E|P\rangle = 0\,. \tag{44}$$

The matrix elements in Eq. (43) involve an integration over the entire $(N+1)$-electron coordinate space, including the radial coordinate r of the Rydberg electron, in analogy to the usual CIT.[6] In Eq. (44) we only integrate over the coordinates of the channel state $|\alpha_0\rangle$, and this defines a second-order differential equation for the radial function $F_E(r)$ which has the asymptotic properties expressed in Eq. (12a). Using the homogeneous solutions of Eq. (44) we obtain the result[7]

$$-\tan\pi\lambda_P G_I(\epsilon, r') = \tfrac{1}{2}\pi B_P(E)\left(\psi_R^0(r') \int_{r'}^\infty dr\, \psi_I^0(r) \frac{r^2}{r} (\langle\alpha|H_T|P\rangle + O)(N+1)^{1/2} + \psi_I^0(r') \int_0^{r'} dr\, \psi_R^0(r) \frac{r^2}{r} (\langle\alpha|H_T|P\rangle + O)(N+1)^{1/2}\right)\,. \tag{45a}$$

Note that both $\langle\alpha|H_T|P\rangle$ and O are functions of the radial coordinate r. The operator O represents the contribution of the $(N+1)$ electron exchange terms to the solution of Eq. (44). These terms are, of course, implicit functions of F_E in Eq. (39). We shall assume that the *exchange* terms in Eq. (45a) are well approximated using $F_E \approx \psi_R^0$. In the limit, as $r\to\infty$, the first integral vanishes, and the second integral is equivalent to V_P in Eq. (40). This should be an excellent approximation in most cases, and is certainly consistent with the assumption that W_P in Eq. (41) can be neglected. Comparing the asymptotic form of Eq. (45a) to Eqs. (39a) and (39b), we obtain the result,

$$-\tan\pi\lambda_P \cong \tfrac{1}{2}\pi B_P(E)\,V_P \tag{45b}$$

and from Eq. (43) we find

$$B_P = V_P/(E-\overline{E}_P) \tag{46}$$

such that

$$-\tan\pi\lambda_P = \frac{\pi}{2}\,\frac{V_P^2}{E-\overline{E}_P} \equiv \frac{\Gamma}{2(E-\overline{E}_P)}\,. \tag{47}$$

If more than one perturbing level were included in Eq. (36), *the right-hand side of Eq.* (47) *would consist of a sum of such resolvent terms.*

Using these results in Eq. (36), we obtain

$$|E\rangle = |\alpha_0;\psi_R^0\rangle + [V_P/(E-\overline{E}_P)](\tfrac{1}{2}\pi V_P|\alpha_0;G_I\rangle + |P\rangle) \tag{48}$$

$$\underset{r\to\infty}{\sim} (1/\cos\pi\lambda_P) \times [|\alpha_0;f\rangle\cos\pi(\xi_0+\lambda_P) - |\alpha_0;g\rangle\sin\pi(\xi_0+\lambda_P)]\,. \tag{49}$$

From the asymptotic properties of Eq. (49), we derive a "quantum defect" $\mu_P(\epsilon)$ for the perturbed series,

$$\cot\pi\mu_P = [\cot\pi(\xi_0+\lambda_P) + \mathcal{G}\,]/A\,, \tag{50}$$

which yields Eq. (5). This is to be compared to the result, Eq. (25), for the unperturbed series. In order to evaluate the important parameter Γ in Eq. (47), we must discuss the proper normalization of the Rydberg functions.

IV. EVALUATION OF Γ AND NORMALIZATION OF THE PERTURBED RYDBERG SERIES

The "width" parameter $\Gamma = \pi V_P^2$ depends on the "reduced" CI matrix element $V_P(E)$ in Eq. (40) and is an analytic function of the total energy E. The *ab initio* calculations provide matrix elements, $\langle E_n^0|H_T|P\rangle$, between the normalized, *unperturbed*, Rydberg wave functions $|E_n^0\rangle$ given in Eqs. (25) and (26), and the normalized, perturbing valence state, $|P\rangle$, in Eq. (34). These are listed in column 5 of Table I for the Cd series. The reduced matrix element, at the specific energies E_n^0 can be determined by the relationship, $\langle E_n^0|H_T|P\rangle \equiv (N_n^0\mathcal{C})\,V_P(E_n^0)$. The normalization for the *unperturbed* wave function, i.e., $(N_n^0\mathcal{C})^2$, is obtained from Eq. (53) with $\nu_n = \nu_n^0$, and $\lambda_P = 0$. The final result is

$$\Gamma = \pi V_P^2 = \pi\langle E_n^0|H_T|P\rangle^2 \times\left[A\left(\frac{\sin^2\pi\xi^0}{\sin^2\pi\mu^0}\right)\left(\nu_n^{03} + 2\,\frac{\partial\mu^0}{\partial E_n^0}\right)\right]\,. \tag{51}$$

The normalization factor in brackets is often well approximated as $[\nu_n^3/A]$. We expect that $\Gamma(E_n^0)$ is only a slowly varying function of the total energy. This is demonstrated by the calculated widths obtained from Stevens' CI matrix elements[1] for Cd given in Table I.

The perturbed wave function in Eq. (48) is *not* normalized. Let $\psi_E = N_E|E\rangle$ such that $\langle\psi_E|\psi_{E'}\rangle = \delta(E-E')$, for $E > E_{\alpha_0}$, $\langle\psi_{E_n}|\psi_{E_{n'}}\rangle = \delta_{n,n'}$, for $E_n < E_{\alpha_0}$. The normalization can be evaluated as follows,[8]

$$\langle\psi_E|\psi_{E'}\rangle = N_E N_{E'} \lim_{r\to\infty}\left(\frac{F_E\dfrac{\partial}{\partial r}F_{E'} - F_{E'}\dfrac{\partial}{\partial r}F_E}{E-E'}\right). \tag{52}$$

We find

$$N_E^2 = [\cos^2\pi\lambda_P\sin^2\pi\mu_P/\sin^2\pi(\xi^0+\lambda_P)2B]\,\theta_E^{-1}\,, \tag{53}$$

where $\theta_E = 1$, for $E > E_{\alpha_0}$, and $\theta_E = \tfrac{1}{2}\nu_n^3 + \partial\mu_P/\partial E_n$, for $E_n < E_{\alpha_0}$ and we obtain

$$\psi_E = \frac{1}{(2B\theta_E)^{1/2}}\,\frac{\sin\pi\mu_P}{\sin\pi(\xi^0+\lambda_P)}\,[\cos\pi\lambda_P|\alpha_0,\psi_R^0\rangle - \sin(\pi\lambda_P)(2/\pi V_P)(\tfrac{1}{2}\pi V_P|\alpha_0,G_I\rangle + |P\rangle)]$$

$$\equiv \frac{-1}{(2B\theta_E)^{1/2}}\,\frac{\sin\pi\mu_P}{\sin\pi(\xi^0+\lambda_P)}\left[\frac{(E-\overline{E}_P)|\alpha_0,\psi_R^0\rangle + V_P(\tfrac{1}{2}\pi V_P|\alpha_0,G_I\rangle + |P\rangle)}{[(E-\overline{E}_P)^2 + \tfrac{1}{4}\Gamma^2]^{1/2}}\right]. \tag{54}$$

From Eq. (54) we can derive simple expressions for properties such as the transition moments and evaluate the influence of the perturbing levels on the oscillator strength to both bound-state levels and the photoionization continuum.

V. DISCUSSION OF RESULTS OBTAINED FOR Cd $(5s\,nd)\,^1D$

The accuracy of the theoretical results and the *simplicity* of their application can be demonstrated using *ab initio* pseudopotential calculations provided by Stevens[1] for Cd $(5s\,nd)\,^1D$ interacting with the Cd $(5p^2)\,^1D$ valence states shown in Fig. 1. The results of the variational calculations are summarized in Table I. These can be used to obtain the three parameters, ξ^0, Γ, and $\overline{E}_P$ we require to characterize the entire system.

The term values for the first six members of the unperturbed series $(5s\,nd)$ are given in column 2. Using Eq. (3) we obtain the unperturbed quantum defect μ_0 in column 3, and from these, using Eq. (4), in conjunction with (27) and (28), we extract the parameter ξ^0 listed in column 4. The "philosophy" of the QDT requires this parameter to become a slowly varying, almost constant, function as nd increases. The variational trial function used to calculate this series is most accurately optimized at small n, and the deviation in ξ^0 for $10d$, from what appears to be a stabilized value for $n=7, 8, \sim 9$ is not unexpected. In the application of the present theory we shall choose our parameters from the results for $5s\ 7d$ as the best compromise. Very similar results would be obtained if, say, $5s\ 8d$ had been chosen.

The second parameter Γ should also be an insensitive function of energy since it measures the interaction of the "tight," perturbing valence state with the inner, energy insensitive portion of the unperturbed Rydberg states. The calculated matrix elements $\langle 5s\,nd|H_T|5p^2\rangle$ are listed in column 5 and, of course, these decrease rapidly because of the normalization factor which scales the $5s\,nd$ functions. Using Eq. (51) to reduce these data, e.g., $\Gamma \approx \pi\nu_n^{03}\langle 5s\,nd|H_T|5p^2\rangle/A$, we obtain the relatively constant Γ values in column 6. Again, we shall employ the $7d$ value as the best compromise between increasing n and decreasing accuracy.

The third parameter $\overline{E}_P$ is given by Eq. (42). We are not prepared to evaluate the shift implied by the quantity $W_P V_P$, and the unshifted value $E_P = 0.07694$ calculated by Stevens will be employed. Various elaborate hand waving arguments can be used to rationalize this *assumption*, but the excellent results we obtain for Cd are, for the moment, the best justification. Obviously, if E_P were to occur, not *above* the ionization limit, but imbedded in the Rydberg series, the exact position $\overline{E}_P$ is more critical, and $\overline{E}_P$ might best be used as an adjustable parameter.

The results of the calculations are given in Table II. Column 2 lists the experimentally observed term values for the $^1D_2$ series.[9] Column 3 lists the predictions of the single configuration variational calculations obtained by Stevens, and column 4 gives the results of solving a (7×7) CI secular equation for the interaction of $5d \rightarrow 10d$ with the $5p^2$ term located at $+8443\ \mathrm{cm}^{-1}$. Obviously the CI calculations make a significant improvement in the eigenvalues.

The result of the present theory is shown in columns 5, 6, and 7. Given a value for Γ, $\overline{E}_P$, and ξ^0, we must evaluate $\lambda_P(E)$, $A(E)$, and $\mathcal{G}(\nu,l)$ from Eqs. (47), (23), and (24), respectively, at some value of E. These quantities are then used in Eq. (50) to arrive at an estimate for $\mu_P(E)$. Ideally this process should be iterated until E agrees with the predicted eigenvalue, E_n, i.e.,

$$E_n = [n - \mu_P(E_n)]^{-2} \qquad (55)$$

As a good first approximation we may evaluate $\mu_P(E_n^0)$ at the "unperturbed" eigenvalue E_n^0. This result is given in column 5 using the parameters Γ and ξ^0 obtained for each individual nd state in Table I. Column 6 shows the results obtained from the $7d$ parameters which we have chosen as the "best" set based on the quality of the calculations employed by Stevens[1]. (The resultant quantum defects are shown by the dashed curve in Fig. 2.) Finally column 7 presents the results of the present theory when the experimental energies E_n in column 1, are employed to evaluate $\lambda_P(E_n)$, $A(E_n)$, and $\mathcal{G}(\nu_n,l)$. This is essentially just a lazy way to achieve the self-consistency required by Eq. (55). In the absence of experimental data essentially the same results would be achieved from a single iteration of Eq. (55) with E_n replaced by $[n - \mu_P(E_n^0)]^{-2}$.

The resultant quantum defects for each level are plotted in Fig. 2. The solid curve is drawn through the predicted values obtained from column 7, using the $7d$ parameters. The circles are the experimentally observed values, and these seem to converge on the theoretical curve. Some of the deviations may be due to "other" unknown perturbations which may interact weakly with the $^1D_2$ series.

The boxes in Fig. 2 indicate the quantum defects obtained from the (7×7) CI results in column 4. The serious deviations one obtains as n increases demonstrates the limitations of using a "truncated" basis for the unperturbed series. Effectively the theoretical expressions derived from QDT yield an *analytic* solution to the *infinite* CI

TABLE II. Comparison of experimental and calculated term values for Cd $(5s\ nd)\,^1D_2$.

	Expt. (cm^{-1}) (E_n)	Calc. unperturbed series (E_n^0)	Results of (7 × 7) CI	Results of QDT		
				Using (*nd*) and E_n^0	Using (7*d*) and E_n^0	Using (7*d*) and E_n
5*d*	−13 320.3	−11 907	−13 004	−12 862	−12 636	−12 552
6*d*	−7 405.3	−6 713	−7 250	−7 301	−7 239	−7 205
7*d*	−4 701.7	−4 309	−4 592	−4 653	−4 653	−4 640
8*d*	−3 243.1	−2 998	−3 162	−3 220	−3 226	−3 221
9*d*	−2 370.6	−2 204	−2 308	−2 361	−2 362.0	−2 359.6
10*d*	−1 804.3	−1 686	−1 749	−1 798	−1 801.3	−1 800.2
11*d*	−1 419.3				−1 416.8	−1 417.3
12*d*	−1 145.4				−1 143.9	−1 144.2
13*d*	−943.5				−942.7	−942.8
14*d*	−790.6				−789.9	−790.1
15*d*	−671.9				−671.6	−671.6
16*d*	−578.18					−577.90
17*d*	−502.61					−502.46
18*d*	−440.95					−440.87
19*d*	−389.92					−389.94
20*d*	−347.38					−347.34
21*d*	−311.30					−311.35
• • •						
23*d*	−280.76					−280.68
24*d*	−231.45					−231.51
25*d*	−211.56					−211.63
26*d*	−194.12					−194.20
∞	0					
p^2		+8 443	+10 695			

secular equation, *including* the contribution of the Rydberg continuum states. The *ab initio* calculations should obviously be directed at obtaining a highly optimized Rydberg wave function at some modest n value in order to obtain the best ξ^0 and Γ values, rather than expanding calculational resources on obtaining a large number of less accurate Rydberg states.

There are, of course, possible contributions from higher-lying $(5p\ np)\,^1D_2$ Rydberg states, of which the so-called valence state $(5p^2)\,^1D_2$ is the lowest, and highly atypical, first member. These states add terms, $\sum_n \Gamma_{P,n}/2(E-E_{P,n})$, to the right-hand side of Eq. (47) which can be evaluated by applying QDT to estimate the widths and positions of the higher states from Γ and $\overline{E}_P$ for the lowest state. However, this rapidly leads us into the next level of theory that must be developed which is a complete generalization of the Seaton multichannel QDT and will be deferred to a later paper. Certainly with regard to the perturbation of the bound states these higher states can be neglected since they are distant, with smaller widths, and any errors introduced will be of the same order as approximating $\overline{E}_P$ by the unperturbed position of the valence state E_P.

We may usually approximate the pre-bracket factors in Eq. (54) simply by $(2\theta_E)^{-1/2}$; the "contribution" of the perturbing $|P\rangle$ state to each, normalized, perturbed Rydberg level is then

$$\frac{G(E)}{\theta_E}=\frac{2}{\pi}\,\frac{\sin^2\pi\lambda_p}{\Gamma\theta_E}\equiv\frac{\Gamma}{2\pi[(E-\overline{E}_P)^2+\frac{1}{4}\Gamma^2]}\,\frac{1}{\theta_E}\,. \tag{56}$$

The quantity $G(E)$ is plotted in Fig. 3 for Cd $^1D_2$. If the entire contribution of the perturbing level were to lie above the ionization limit, where $\theta_E=1$, and E were continuous, we would recognize $G(E)$ as the normalized Lorentzian line shape,

$$\int dE\, G(E)\simeq 1 \tag{57}$$

or, equivalently, as the Fano-Beutler profile[6] associated with the "autoionizing" $|5p^2\rangle$ state.

In view of our neglect of the higher members of the $(5p\ np)\,^1D_2$ series this line shape is only approximate, particularly for $E>\overline{E}_P$, since this resonance will overlap the $(5p\ 6p)$ state at $E\approx 0.27$, which should have a width $\approx\frac{1}{4}\Gamma\approx 0.05$ Ry. The details of such overlapping effects are incidental to the purpose of this paper and can be easily treated in the more general, multichannel approach.

In the present case, the "autoionizing" width, i.e., $\Gamma=2.722$ eV, is sufficiently large that it "extends" below the ionization limit and perturbs the Rydberg series. The contribution to each bound state is

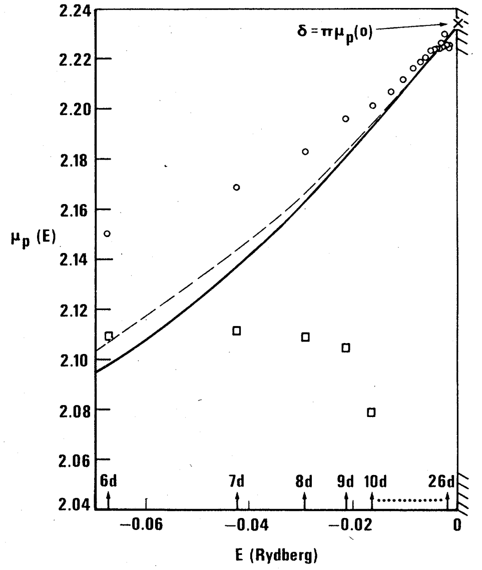

FIG. 2. Quantum defects for Cd $^1D_2$, i.e., $E(nd) = (n-\mu_p)^{-2}$, with $n \geqslant 5$. The circles represent the experimental values obtained by Brown, Tilford, and Ginter (Ref. 8). The dashed curve is the result of the present theory, utilizing the unperturbed eigenvalues E_n^0 as an *initial* guess for E in Eqs. (47), (50), (23), and (24). The solid curve is the result of utilizing the experimental eigenvalues to evaluate the parameters λ_p, A, and $\mathcal{G}$, and closely approximates the final results that would be obtained from an iteration of the theoretical expressions. The squares present the predictions of a (7×7) CI solution using the first six $(5s\ nd)\,^1D$ wave functions and the $(5p^2)\,^1D$ state obtained by Stevens (Ref. 1).

$$G(E_n)/\theta_{E_n} \cong G(E_n)(2/\nu_n^3) .$$

If we may approximate the summation over bound states as follows, we simply recover the normalization condition in Eq. (57), i.e.,

$$\sum_{n=l+1}^{\infty}{}' G(E_n)\frac{2}{\nu_n^3} \cong \int dn\, G(E_n)\frac{2}{\nu_n^3} \approx \int_{-\infty}^{0} dE\, G(E) . \qquad (58)$$

It should be obvious that the present theory is completely equivalent to Fano's CI theory.[6] In fact, Fano has completely summarized the application of CI theory to perturbed Rydberg series when $\bar{E}_P$ lies *below* the ionization limit in Appendix B of his paper and has extracted most of the qualitative features we have discussed. Our contribution has been to generalize his results and obtain quantitative relationships which permit use of calculated CI matrix elements to obtain the pertinent parameters.

VI. SUMMARY AND CONCLUSIONS

We have developed theoretical expressions for the perturbation of a Rydberg series by a single interloping energy level. The interaction can be expressed in terms of a generalized "width" which is easily calculable by variational techniques and allows for simple extrapolation of bound-state calculations into the ionization continuum. The expressions are in complete analogy to Fano's CI theory, but apply equally well to autoionizing states and to configuration interaction in the Rydberg region, below the ionization limit. Even without access to theoretical calculations, Eq. (5) gives a very useful parametric form for analyzing perturbed Rydberg series without restriction to weak interactions and permits treatment of perturbing levels *above* the ionization limit.

The theory can easily be generalized to configuration interaction between many Rydberg series, and explicit relationships can be derived between CIT and multichannel QDT. In this way we can utilize the theoretical apparatus developed for bound-state variational calculations to obtain cross sections for photoionization and autoionization phenomena. Such calculations are particularly imperative for molecular systems where the experimental data is often unavailable or uninterpretable.

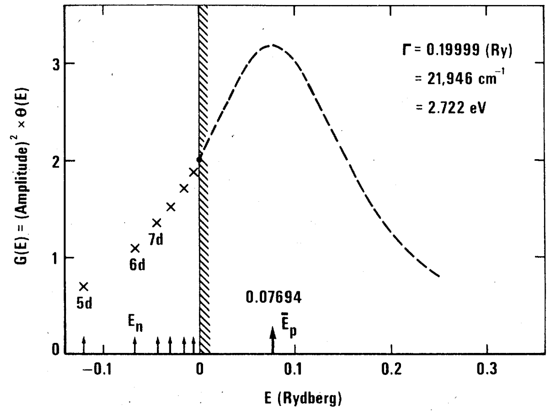

FIG. 3. Contribution of the perturbing Cd $(5p^2)\,^1D$ valence state to the ^1D Rydberg series. $G(E) =$ (amplitude)^2 × $\theta(E)$ measures the (amplitude)^2 of the $(5p^2)\,^1D$ state to the total wave function at energy E. The quantity $\theta(E) = 1$ for $E \geqslant 0$, and the envelope of $G(E)$ represents the usual Fano-Beutler line shape for this autoionizing state. Below the ionization limit, $E < 0$, $\theta(E_n) = \frac{1}{2}\nu_n^3$ weights the contribution of the valence state to the discrete Rydberg states at $E_n = \nu_n^{-2}$.

ACKNOWLEDGMENTS

I especially wish to thank Professor M. J. Seaton and the entire staff of the Physics Department at the University College London for their hospitality, and their many beneficial discussions during my tenure as visiting scientist. I am indebted to Dr. W. J. Stevens for his invaluable assistance in providing the theoretical parameters required in this paper. This research was supported in part by the Office of Laser Fusion, Department of Energy.

---

[1] W. J. Stevens, unpublished MCSCF calculations using the Cd effective core potential of H. Basch *et al.*, J. Chem. Phys. 68, 4005 (1978).

[2] (a) M. J. Seaton, Proc. Phys. Soc. 88, 801, 815 (1966); (b) Comments At. Phys. 2, 37 (1970).

[3] *Handbook of Mathematical Functions*, Natl. Bur. Stand. Appl. Math. Ser. 55, edited by M. Abramowitz and I. Stegun (U.S. GPO, Washington, D. C., 1959), p. 258. Equation (24) is well approximated for $l=2$, by $(A/2\pi)\,\epsilon\,(37/6-1079\epsilon/60+\cdots)$, as $\epsilon\rightarrow 0$.

[4] J. Dehmer and U. Fano, Phys. Rev. A 2, 304 (1970).

[5] N. F. Mott, and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (Oxford University, London, 1965).

[6] U. Fano, Phys. Rev. 124, 1866 (1961).

[7] See Chap. IV of Ref. 5.

[8] This is discussed in Ref. 2(a), pp. 811–814.

[9] C. M. Brown, S. G. Tilford, and M. L. Ginter, J. Opt. Soc. Am. 65, 1404 (1975).