PHYSICAL REVIEW A VOLUME 43, NUMBER 9 1 MAY 1991

# *Ab initio* relativistic many-body calculations for the Hg $6p^2$ resonances

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(Received 19 November 1990; revised manuscript received 11 January 1991)

Relativistic configuration-interaction calculations have been made for the $6p^2$ resonances of Hg I using a relativistic version of the Fano theory. Pair-correlation effects associated with the $5d$ and valence electrons are important, contributing $\sim 1.5$ eV to the positions of the resonances. Relative to Hg $6s^2$, the theoretical positions of the resonances (in $\text{cm}^{-1}$) are 90 654, 94 595, 97 066, 106 257, and 111 609 for $^3P_{0,1,2}$, $^1D_2$, and $^1S_0$. The experimental values are 90 096, 93 980, 96 185, and (tentatively) 103 232, 109 286 $\text{cm}^{-1}$. The theoretical values for the width (in eV) are 0.002, 0.0, 0.215, 0.914, and 0.298. The experimental value for the $^3P_2$ width is $0.272\pm0.074$ eV.

## I. INTRODUCTION

We are seeking to complete the development of a relativistic many-body methodology that will allow us to calculate, fully relativistically, lifetimes of metastable states of atomic negative ions. To date, we have completed the development of the methodology for bound-state functions[1,2] and used these results to predict oscillator strengths for the $\text{Tl}^+$ resonance transitions.[2] In this work, we turn our attention to the generation of relativistic continuum functions, and by making the configuration-interaction in the continuum (CIC) theory[3,4] relativistic, we combine this with the relativistic bound-state methodology[1,2] to predict, for the first time in an *ab initio* manner, the positions and widths of the $6p^2$ resonances of Hg I. These constitute an attractive test, as the $^3P$ levels are well established[5,6] and the $^1D$ and $^1S$ levels are still not completely identified.[7] Additionally, to a substantial extent we are dealing with a two-electron system.

In Sec. II of this work, we outline the relativistic version of the CIC method. Section III discusses the generation of relativistic continuum functions. Section IV tells how the localized (bound) wave function is calculated and Sec. V how relativistic continuum functions are allowed to interact (via relativistic CIC theory) with the localized wave function. Section IV includes discussion of the relativistic REDUCE method[2] used to reduce the number of couplings that must be considered and Sec. V the numerical and analytic methods used to calculate the shifts and widths of the relativistic CIC theory.

## II. RELATIVISTIC CIC THEORY

Since this is our first application of relativistic resonance theory, we shall only introduce concepts and calculation methods that we feel are necessary at this stage to produce reliable results for the resonances of Hg. Later, as circumstances necessitate, we will introduce refinements such as systematic treatment of nonorthonormality, inclusion of localized correlation effects in continuum wave functions, etc., which have already been considered, at times, in the nonrelativistic treatment of resonances (this will also include phenomena that arise solely from relativity as well).

The CIC theory[3] begins with a separation of the problem into a localized (bound) part, and a continuum (continua) part. To the greatest extent possible, we want to deal with an orthonormal problem throughout (nonrelativistically, this requirement has most frequently been relaxed in dealing with the widths). Our choice of how to effect this separation is a relativistic generalization of earlier nonrelativistic work.[4] In the case of the Hg $6p^2$ resonances, enough information is available[5-7] to know that these all lie above the $\text{Hg}^+$ $6s$ threshold and below the $\text{Hg}^+$ $6p$ (hence the resonances are of the Feshbach type) and $\text{Hg}^+$ $5d^9 6s^2$ thresholds. Thus we must[3,4] project out the $6s\ s$ and $6s\ d$ continua in order to apply the theory. Like the nonrelativistic work,[4] we do this at the zeroth-order (Dirac-Fock) level. In particular, we assume that all continua in need of projection can be built from the same $1s, \ldots, 6s$ Dirac-Fock spinors, which are also the same ($1s, \ldots, 5d$) as the ones appearing in the localized portion of the wave function (i.e., this is one assumption of orthonormality). We add a $6s$ to the localized spinor set, which we obtain from a convenient Dirac-Fock calculation—in our case from $\text{Hg}^+$ $6s$. We should state at the outset that most of our bound-state Dirac-Fock spinors are obtained using the program of Desclaux;[8] the remaining bound spinors (those used in continuum function generation) are obtained using the program of Grant and co-workers.[9] The $6s$ spinor is then included in the localized spinor set and, for the most part, all configurations $6s\ s$ and $6s\ d$ are excluded from the localized wave function. In the following, we use, for example, the notation $6s\epsilon s$ for a continuum subshell ($\epsilon s$), $6sns$ for a discrete (bound) subshell ($ns$), and $6s\ s$ when either is meant. This not only projects out, to zeroth order,[4]

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the continua (open channels, $6s\epsilon s$ and $6s\epsilon d$), but the denumerably infinite discrete series $6snd_j$ (two of them) and $6sns$ that lie below the resonances. These discrete Rydberg series can be formally reintroduced within the context of the theory (correctly through first-order perturbation theory), and this is certainly "numerically convenient." However, in Sec. V we shall demonstrate that at least as far as the width of the $J=2$ resonances are concerned this is not adequate.

Once the localized function is constructed (see Sec. IV), the next concern of the CIC theory is the construction of continuum wave functions that, hopefully will be satisfactorily orthonormal. In the present case, these are constructed by doing frozen-core relativistic Dirac-Fock continuum calculations for $6s\epsilon s$ ($J=1$), $6s\epsilon d_3$ ($J=1,2$), and $6s\epsilon d_5$ ($J=2$). This notation implies the following.

(i) The $s$ relativistic continuum spinor is calculated from the $^3S_1$ coupling and that spinor is then used for the $^1S_0$ continua. The problems[10] associated with the use of a single configuration and an orthogonal spinor set are thus avoided. The same approach was used for the discrete $6sns$ spinors, although in this case it was necessary to modify Desclaux's program,[8] by setting the $6sns$ Lagrange parameter to zero, in order to generate the $J=1$ solution.[2]

(ii) In the case of the $d$ spinors, the coupling implies that we assumed that there was very little interaction within or between $\epsilon d$ channels. This was checked by examining "high-$n$" matrix elements, viz., $\langle 6snd|H|6smd\rangle$. It was found that within a channel these were $10^{-5}$ or less in magnitude and that between channels ($J=2$) matrix elements were $10^{-3}$ or less in magnitude. For the calculation reported here, this was considered adequate.

Formally, the localized basis function $\phi$ and the continuum wave functions $\psi_E$ form an orthonormal set and the shift of the localized energy ($E_\phi=\langle\phi|H|\phi\rangle$) is given by

$$E-E_\phi=\sum_{n,i}\frac{|\langle\phi|H|\psi_{ni}\rangle|^2}{E-E_{ni}}+\sum_i \mathrm{P}\int dE_i'\frac{|\langle\phi|H|\psi_{E_i'}\rangle|^2}{E-E_i'}\,, \tag{1}$$

where the sums are over all open channels ($6s\epsilon s$ for $J=0$; $6s\epsilon s, 6s\epsilon d_3$ for $J=1$; and $6s\epsilon d_3, 6s\epsilon d_5$ for $J=2$), P indicates a principal-value integral, $\psi_E$ ($\psi_n$) are the open channel continuum (discrete) wave functions, and $E-E_\phi$ is the desired shift.

The full width $\Gamma$ of the resonances, which is inversely proportional to its lifetime, is given by the equation ("golden rule")

$$\Gamma(E)=2\pi|\langle\phi|H-E|\psi_E\rangle|^2\,, \tag{2}$$

which is to be evaluated at the "final" position of the resonance.

## III. GENERATION OF RELATIVISTIC CONTINUUM ORBITALS

Relativistic continuum orbitals are generated[11,12] within the frozen-core approximation. The expression for the energy is electrostatically correct for each level in question (no Breit effects are included), and the off-diagonal Lagrange parameters are fully included. This approach is analogous to the nonrelativistic one used by Bates.[13] The mesh is a combination of the exponential grid used by Desclaux[8] for the first few hundred points, and a linear grid spaced so there are at least six grid points per half cycle of oscillation (current dimensioning is limited to 2000 points so that orbital energies must be $\leq 100$ a.u.). In the "match region" a rational function interpolation and/or extrapolation procedure is applied to allow the integration to continue smoothly from the exponential to the linear mesh.

The bound spinors are obtained from either the Grant[9] or Desclaux[8] programs. Integration of the continuum equation proceeds until the asymptotic region is reached (exchange potentials effectively zero). Normalization then proceeds via the Stromgren method,[14,15] which applies a WKB approach to the major component of the relativistic continuum function. This agreed quite well for the relativistic hydrogenic cases for $Z\leq 60$, where both components were asymptotically fit to the regular and irregular confluent hypergeometric solutions.

The off-diagonal Lagrange parameters $\gamma_{ij}$ are calculated in a somewhat novel way. One inputs estimates for them ($\gamma_{ij}=0$), solves for the continuum orbital, calculates the orthogonality integrals, and uses these results to estimate new parameters by the bisection method. Thus one is able to avoid having to input specific information concerning the Dirac-Fock equations used to construct the bound spinors, in contrast to the nonrelativistic procedure.[13]

## IV. CONSTRUCTION OF THE LOCALIZED WAVE FUNCTIONS

One begins by solving[8] the Dirac-Fock (DF) equations for the $6p^2$ resonances and the $6s^2$ reference state of Hg I. The correct electrostatic structure for each level is used[16] with the average energy Breit contributions; the results are shown in Table I. Since the contribution of the average Breit energy to energy differences is less than 0.5 mhartree, and because the valence-valence radial Breit integrals are one to two orders of magnitude smaller than the largest ones in the average energy, one concludes that nonaverage Breit effects can be ignored for the energy differences.

Table I also contains the DF [more properly, the multiconfigurational Dirac-Fock (MCDF)] coefficients. It is possible to determine how "pure" these are from an $LS$ perspective by forming $LS$ eigenstates[1,2] from the $jj$ coupled configurations and then expressing the MCDF results in terms of these $LS$ states. The result is that the "$^3P$"$_2$ state has a 21% admixture of $^1D_2$ in it, while the "$^3P$"$_0$ state, at the MCDF level has an admixture of 6.7% of $6p^2\,{}^1S_0$ in it. Without this admixture, the "$^3P$"$_J$ state would not interact with the continuum (via the Coulomb operator), so that we would have bound states rather than resonances (the "$^3P$"$_1$ state is pure at the MCDF level, so it is bound at this level). As we shall see when we calculate the widths, the large admixture of $^1D_2$ in the "$^3P$"$_2$ state produces a "broad" state, whereas "$^3P$"$_0$ remains quite sharp, due to the small admixture of $^1S_0$ in it. Finally, the "$^1D$"$_2$ state is 21% $^3P_2$ and the "$^1S_0$" state is 6.3% $^3P_0$.

Once the zeroth-order wave function (MCDF) is avail-

TABLE I. MCDF and Breit energies (a.u.) and coefficients. (In designating relativistic subshells, we use $2j$ and not $j$ as a subscript throughout this work.)

| | | | Coefficients | | |
|---|---|---|---|---|---|
| State | $E_{\mathrm{Breit}}$ | $E_{\mathrm{MCDF}}$ | $6p_1^2$ | $6p_1 6p_3$ | $6p_3^2$ |
| $6p^2\,{}^1S_0$ | 22.593 825 3 | −19 625.824 177 0 | −0.352 79 | | −0.935 70 |
| $6p^2\,{}^1D_2$ | 22.593 857 6 | −19 625.863 808 5 | | 0.463 58 | −0.886 05 |
| $6p^2\,{}^3P_2$ | 22.594 035 9 | −19 625.894 569 2 | | 0.887 08 | 0.461 616 |
| $6p^2\,{}^3P_1$ | 22.594 109 3 | −19 625.906 012 4 | | 1.0 | |
| $6p^2\,{}^3P_0$ | 22.594 297 4 | −19 625.920 164 7 | −0.938 56 | | 0.345 123 |
| $6s^2\,{}^1S_0$ | 22.594 095 8 | −19.626.275 315 6 | | | |

able, the many-body wave function is constructed[1,2] from those configurations characteristic of a first-order wave function (single or double subshell excitation from at least one configuration present in the Dirac-Fock solution). The wave function is further restricted to only permit excitation from the $n=5$ and 6 subshells of the solution [excitations from other shells are thought to contribute little to the properties of these resonances (see below)].

While the $6p^2$ resonances lies below the $\mathrm{Hg}^+$ $5d^9 6s^2$ continua, bound configurations of the type $5d^9 6s^2 nl$ where $nl=7s$, or $6d$ lie between the Hg $6p^2$ resonances.[5-7] Neither of these configurations was allowed to appear in our energy matrices, because they are related by triple excitation, viz., $5d6p^2 \rightarrow 6s^2 nl$ to the dominant configuration ($6p^2$), and so do not directly interact with the MCDF solution.

Subshells unoccupied in the zeroth-order function are called "virtual" subshells, and the radial parts of the spinors associated with them are represented by relativistic screened hydrogenic functions whose screening constants are optimized using the energy variational principal. As argued in our earlier work[2] and further evidenced here through the numerical results, use of such functions seems to properly couple the major and minor components to prevent collapse into the "positron" sea (for a discussion of this problem see Ref. 17 and for other remedies see Ref. 18) if the variations are done with some care. In particular, we find, just as in the nonrelativistic cases (e.g., Ref. 19), that a very good *estimate* of the effective charge of the virtual radial function can be made by forcing it to produce the same average value of $r$ as the Dirac-Fock spinor it is replacing (formulas are available in the literature[20,21] for $\langle r \rangle$). Final values of the effective charges are determined during application of the energy variational principle.

To date, the choice of $n=l-1$ ($l$ is the orbital quantum number of the major component) for the virtual radial function's power of $r$ has been most effective. When a second virtual radial function is needed for the same shell, we increase $n$ by one unit (to avoid degeneracy problems). This choice of $n$ differs from that used nonrelativistically;[19] there, $n$ had a value corresponding to the lowest unoccupied subshell of the appropriate symmetry ($n=7$ for $s$ and $p$ functions, $n=6$ for $d$, and $n=5$ for $f$ and $g$ functions). But in the nonrelativistic case, the $n>l-1$ virtual radial functions were a single Slater-type orbital (STO), whereas relativistically, hydrogenic virtuals with $n>l-1$ consist of more than one term. This may account for the differences we encounter in choosing $n$ (clearly a study of both the nonrelativistic and relativistic cases would be of interest).

Our experience (Ref. 19 and this work) and relativistic experience to date suggest that two optimized relativistic screened hyrogenic functions per $l$ are sufficient to generate about 90% of the pair-correlation energy. The following considerations apply to determine at which $l$ to truncate the virtual subshell space.

(i) Strict application of first-order perturbation theory to all single and double excitations (except double excitation into two virtual subshells) requires that the $j$ subscript of the virtual be no greater than $3j_{\max}$, where $j_{\max}$ is the largest $j$ in the zeroth-order wave function associated with the "active subshells." This limits the virtual subshell's $l$ to $\leq 3j_{\max}+\frac{1}{2}$. For example, for the $6p^2$ pair energy, $l$ would be $\leq 5$.

(ii) On the other hand, for the $6p^2$ case, the nonrelativistic limitation[19] would be $3l_{\max}=3$. It has also been found nonrelativistically[19] that the "bivirtual" correlation (double excitation into two virtual subshells) can also have this restriction applied to it.

(iii) For the relativistic calculations reported here, we have chosen to cut off the virtual symmetry at $l=4$. This choice was based on computational evidence from our nonrelativistic Hg studies (see below).

The choice of what pair correlation to include from the "core" depends on the choice of reference state that is made. In the present context, Hg I $6s^2\,{}^1S_0$ was chosen as a reference. Nonrelativistic computational evidence[22,23] suggests that the pairs, in order of their importance in contributing to the energy difference between Hg $6p^2$ and Hg $6s^2$, are $5d6p, 6p^2$ followed by $5d^2, 5p6p, 5s6p$ (the last three are not necessarily in order). The core-valence pairs ($5l, 6l'$) present two difficulties not present in the valence pairs ($6s^2, 6p^2$).

(i) They involve a lot more "parents" per configuration, due to the opening of the $5d$ subshell.

(ii) They (and other pairs involving $5d$; in particular, $5d^2$) possess a large pair energy (for example, the $5d,6p$ pairs for "${}^3P_2$" have nearly 1.50 eV of energy), which must be calculated so that the errors that have been made nearly cancel out. We either have to make our absolute error 5%, or so, or make sure that all $5d,6p$ and $5d,6s$ pairs have similar errors so that energy differences between these pairs are accurate to a few hundredths of an eV. This involves, among other things, making sure that comparable virtual subshell sets are used, that the same variety of configurations are included (e.g., the same $l$ truncations are used), and that *all* the parents associated with each configuration are *carefully* screened.

This last point initially presents some difficulties in that there are several thousand possible parents, but we desire to keep our energy matrices to $\sim 300$ parents due to the lack of a multiroot large diagonalizer and for reasons of analysis and interpretation. To overcome this, we initially introduced the relativistic REDUCE method.[2] As applied here, we take the MCDF solution as our zeroth-order function and then the energy matrix element between the MCDF solution and each virtual configuration is written out symbolically[16] in terms of the $M$ electrostatic $R^k$ integrals (and one-particle integrals in some of the single excitation cases). Most frequently ($J=0$ is an exception) there are fewer of these integrals than there are parents ($N$). The program[24] then rotates the parental set to a new orthonormal set having $N-M$ parents, which have zero matrix element with the MCDF solution. These $N-M$ new parents are then discarded. Reductions of a factor of 3 or more were observed in this work (e.g., for $5d,6p \rightarrow vd,vf$ in $^3P_1$ we went from 118 parents to 42 parents). But these also prove to be too many survivors. We then break the problem up, investigating a subset of the $5d,6p$ (or $5d,6s$) parents in the presence of the $6p^2$ ($6s^2$) correlation. Small parents (energy contribution $<0.015$ mhartree in magnitude, providing the coefficient is smaller than 0.003) are then removed. After all the sections have been investigated, the survivors are reassembled in a single final run. The final-energy matrices have about 300 parents for each level. Calculation times on a SUN Sparc 1 are about 30–40 min for the final run (iteration of the virtual radial functions occurs during the "sectioning" process).

In Table II, we present our final values for the many-body energy associated with pair excitations from $6p^2$, $6s^2$, $5d6p$, and $5d6s$, and the single-excitation $5d \rightarrow vd + vg$, which is absent in the reference state. The many-body energy is divided among various symmetry classifications, using intermediate normalization, $\langle \phi | \psi \rangle = 1$, where $\phi$ is the MCDF reference function and $\psi$ is the complete function. In this context, according to first-order perturbation theory,[18] each parent contributes to the many-body energy: $(C_p/C_0)^* \langle \phi | H | P \rangle$ where $C_p$ ($C_0$) is the parent's (reference function's) coefficient in $\psi$ and $\langle \phi | H | P \rangle$ is the off-diagonal matrix element connecting the parent and the reference function. While this first-order analysis is very useful, there are obvious cases where it is not valid; for example, when a parent raises the energy, according to the analysis. This merely implies that higher-order effects dominate.

As we can see from Tables II and III, the most significant effect of the $5d,6p$ ($5d,6s$) correlation is to considerably increase (by 1.3–1.7 eV) the $6p^2$-$6s^2$ "gap." The near uniformity of this increase, which is expected based on our nonrelativistic experience (Refs. 22 and 23 and Table III), occurs within each symmetry category. This characteristic presents us with a good "diagnostic" test—if there were any significant discrepancies, then one should reexamine the completeness of the various basis sets used (virtual subshell, parental, configurational), to make sure no large contributions were missed (this was done for all the entries in Table II).

TABLE II. Contributions to correlation energy by symmetry pair (in mhartree).

|  | $6p^2$ |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| $\epsilon_{6p^2}$ | "$^3P$"$_0$ | $^3P_1$ | "$^3P_2$" | "$^1D$" | "$^1S$" | $\epsilon_{6s^2}$ | $6s^2\,{}^1S$ |
| $s^2$ | $+1.740$[a] |  |  |  | $+3.500$[b] | $s^2$ | $-0.900$ |
| $p^2$ | $-1.269$ | $-0.824$ | $-1.123$ | $-0.969$ | $-4.808$ | $p^2$ | $-16.092$ |
| $d^2$ | $-3.657$ | $-2.765$ | $-2.935$ | $-2.985$ | $-13.638$ | $d^2$ | $-0.912$ |
| $f^2$ | $-1.044$ | $-0.571$ | $-0.589$ | $-0.621$ | $-3.513$ | $f^2$ | $-1.143$ |
| $g^2$ | $-0.188$ |  | $-0.060$ |  | $-0.852$ | $g^2$ | $-0.297$ |
| $sd$ |  |  | $-0.603$ | $-1.664$ |  | $6s \rightarrow s$ | $\sim 0$ |
| $pf$ |  |  | $-0.049$ | $-0.177$ |  | $\epsilon_{5d6s}$ |  |
| $dg$ |  |  | $-0.609$ | $-0.290$ |  | $sd$ | $-13.733$ |
| $6p \rightarrow p$ | $-0.035$ | $-0.788$ | $-1.630$ | $-0.519$ | $-0.0350$ | $pf$ | $-62.492$ |
| $f$ |  |  | $-1.345$ | $-2.475$ |  | $dg$ | $-4.954$ |
| $\epsilon_{5d,6p}$ |  |  |  |  |  | $p^2$ | $-17.768$ |
| $sp$ | $-4.504$ | $-4.395$ | $-4.198$ | $-4.084$ | $-4.276$ | $d^2$ | $-0.137$ |
| $pd$ | $-10.965$ | $-8.778$ | $-7.051$ | $-7.114$ | $-7.117$ | $f^2$ | $-1.576$ |
| $df$ | $-18.267$ | $-18.067$ | $-16.493$ | $-15.509$ | $-14.430$ | $g^2$ | $-0.211$ |
| $fg$ |  |  | $-0.460$ | $-0.613$ |  | $5d \rightarrow d$ | $\sim 0$ |
| $sf$ | $-19.055$ | $-16.775$ | $-16.031$ | $-12.287$ | $-14.084$ | $5d \rightarrow g$ |  |
| $5d \rightarrow d$ | $-2.770$ | $-3.512$ | $-3.079$ | $-2.577$ | $-1.176$ |  |  |
| $g$ | $-1.139$ | $-0.957$ | $-1.018$ | $-0.972$ | $-1.147$ |  |  |

[a] $6s^2 = +1.888$.

[b] $6s^2 = +6.249$.

TABLE III. Contributions to correlation energy by origin in (mhartree).

| | | | $6p^2$ | | | | $6s^2$ |
|---|---|---|---|---|---|---|---|
| | "$^3P$"$_0$ | $^3P_1$ | "$^3P$"$_2$ | "$^1D$"$_2$ | "$^1S_0$" | $^1S_0$ | |
| $\epsilon_{6p^2}$ Rel.[a] | −4.453 | −4.948 | −8.943 | −9.69 | −19.346 | $\epsilon_{6s^2}$ Rel.[a] | −19.344 |
| $\epsilon_{6p^2}$ NR[b] | −4.710 | −4.710 | −4.710 | −9.241 | −16.275 | $\epsilon_{6s^2}$ NR[b] | −22.024 |
| $\epsilon_{5d,6p}$ Rel.[a] | −52.791 | −48.015 | −44.233 | −39.607 | −39.907 | $\epsilon_{5d,6s}$ Rel.[a] | −100.871 |
| $\epsilon_{5d,6p}$ NR[b] | −41.313 | −41.313 | −41.313 | −40.487 | −37.654 | $\epsilon_{5d,6s}$ NR[b] | −69.914 |
| $\epsilon_{5d}{}^c$ Rel.[a] | −3.909 | −4.469 | −4.097 | −3.549 | −2.323 | $\epsilon_{5d}{}^c$ Rel.[a] | ~0 |
| $\epsilon_{5d}{}^c$ NR[b] | | | | | | $\epsilon_{5d}{}^c$ NR[b] | |
| $\epsilon_{5p6p}$ NR[b] | −2.294 | −2.294 | −2.294 | −2.221 | −1.936 | $\epsilon_{5p,6s}$ NR[b] | −5.863 |
| $\epsilon_{5s6p}$ NR[b] | −0.129 | −0.129 | −0.129 | −0.0990 | −0.0567 | $\epsilon_{5s,6s}$ NR[b] | −0.4907 |

[a] From Table II.

[b] Separate nonrelativistic calculations (this work).

[c] Single excitations from $5d$.

The valence contributions vary more among the resonance states because (i) a contribution may be excluded in one resonance and present in another (e.g., *vpvf*) for reasons of symmetry; (ii) many-body effects may be more nearly degenerate for one resonance than another (i.e., many-body configurations may be closer to the MCDF configurational energy in one case than in another).

The main source of error in Table II is associated with the $5d,6p$ ($5d,6s$) pair energies and arises from at least three causes: (i) truncation of the parental space (parents contributing $<0.015$ mhartree have been excluded); (ii) incomplete radial space (primarily failure to use a second set of virtuals for the $5d,6l$ correlation); and (iii) truncation of the angular space, e.g., exclusion of *fg* (in some cases), *pg* (in all cases), and all $l>4$ correlations.

In Table IV, we provide estimates of these three error types. It is of interest to note that in the case of the "$^1D$" the use of extra virtuals actually *raised* the energy somewhat (~2 mhartree). This appears to involve a third-order effect for a root that is not the lowest in the matrix.

There are other errors associated with Table II as well. For example, we neglected the contribution of the Breit operator within the $5d \rightarrow vd$ excitation. For the "$^3P$" levels, core-valence effects might provide a significant "shielding" of the bare-nucleus effects from this source.

As part of this project, we undertook nonrelativistic calculations as well. Originally, these were used as indicators to give us an idea of what configurations should be included. We have cited the final results of this study in Table III (more detail can be found in Ref. 23). The nonrelativistic results (see Table III) follow the relativistic ones fairly closely. Thus we may anticipate that when the $5p,6l$ correlation is obtained relativistically, the $6p^2$-$6s^2$ gap may be widened by about 3.5 mhartree and that the effect of the $5s,6l$ correlation will be $<0.4$ mhartree (widening the gap). Nonrelativistic studies may be continued in the future for the $5d^2$ correlation to estimate the size of the relativistic contributions from these excitations (these calculations are difficult to perform relativistically currently). The present nonrelativistic calculations also indicate that *vpvg* symmetries contribute $<0.8$ mhartree to $5d,6p$ pairs, and that *vf vg* contributions should

TABLE IV. Total energies (add −19 625.0 hartree to get absolute values) (in hartrees).

| Source | "$^3P$"$_0$ | $^3P_1$ | "$^3P$"$_2$ | "$^1D$"$_2$ | "$^1S$"$_0$ | $6s^2\,{}^1S_0$ |
|---|---|---|---|---|---|---|
| MCDF[a] | −0.920 165 | −0.906 012 | −0.894 569 | −0.863 807 | −0.824 177 | −1.275 316 |
| Corr.[b] | −0.061 153 | −0.057 432 | −0.057 273 | −0.052 85 | −0.061 576 | −0.120 215 |
| Errors[c] | −0.001 49 | −0.001 39 | −0.0161 | +0.002 23 | −0.000 043 | 0.0 |
| Open channels[d] | +0.000 030 | 0.0 | −0.000 13 | +0.002 69 | −0.001 35 | 0.0 |
| Down shift[e] | 0.0 | 0.0 | 0.0 | 0.0 | −0.000 22 | 0.0 |
| Total[f] | −0.982 778 | −0.964 834 | −0.954 582 | −0.911 737 | −0.887 366 | −1.395 531 |
| Total ($6s^2$)[g] | +0.412 753 | +0.430 696 | +0.441 948 | +0.483 794 | +0.508 165 | 0.0 |
| Total (cm$^{-1}$)[h] | 90 654 | 94 595 | 97 066 | 106 257 | 111 609 | 0.0 |
| Expt. (cm$^{-1}$)[i] | 90 096 | 93 980 | 96 185 | 103 232 | 109 286 | 0.0 |
| Error (eV)[h,i] | 0.069 | 0.076 | 0.109 | 0.375 | 0.288 | 0.0 |

[a] From Table I.

[b] From Table II (total correlation).

[c] Estimated errors due to truncating parental and radial basis from $5d,6p$ pairs (see text).

[d] See Sec. V.

[e] Adding $=-0.029\,25$ hartree to the $6s^2$ diagonal matrix element (see text).

[f] Sum of a through e.

[g] Energies relative to $6s^2$ (f).

[h] Converting hartree to cm$^{-1}$. Using 1 a.u.$=27.211\,396$ eV and 84 184.1 cm$^{-1}=10.43$ eV.

[i] Refs. 5–7. The "$^1S$" and "$^1D$" assignments are tentative.

be closer to 2.0 mhartree (rather than 0.5 mhartree, as indicated in Table II); this suggests the need of an additional $vg$ for the $5d,6p$ pairs.

Finally, to account (in part) for the difference between the Hg$^+$ $6s$ and Hg $6s^2$ spinors, we added $-0.02925$ hartree to the $6s^2$ diagonal matrix element (in $6p^2$"$^1S$"$_0$), which was built from the Hg$^+$ $6s$ spinor (this properly accounted for the diagonal element). As can be seen from Table IV, the effect was small.

## V. CALCULATION OF SHIFTS AND WIDTHS OF RESONANCES

The shifts are evaluated self-consistently using Eq. (1), taking as an initial starting point $E=E_\phi$, i.e., the localized energy (referenced to Hg $6s^2$) from Sec. IV. To solve this equation we initially made several approximations.

(i) To evaluate the off-diagonal matrix elements (both discrete and continuum channels) only MCDF wave functions were used (this was relaxed for the width; see below).

(ii) The Breit operator was not included in the off-diagonal matrix elements.

(iii) We assumed that the radial parts of the MCDF wave functions of the localized portion of the resonance states did not vary much from state to state so that we did not have to calculate an $R^k$ integral repeatedly for different resonance states.

(iv) We assumed that the discrete and continuum open-channel radial functions are independent of the final $J$ (see Sec. III for more detail).

All these approximations greatly simplify the calculation, which ends up requiring 30–50 points to cover the energy range from 0 to 5 a.u. for each set of integrals: $R^k(6p^2;6s\epsilon d_3)$, $R^k(6p^2;6s\epsilon d_5)$, and $R^k(6p^2;6s\epsilon s)$. Calculation times for each point are about 1 h on a SUN Sparcstation 1.

Two of the approximations were checked directly in this work. For (3), for example, in calculating the shifts for "$^3P$"$_2$ and "$^1D$"$_2$, we used the proper MCDF radial functions for each level, and found that the radial integrals used to calculate the shift only changed about 5%. To check approximation 4, we ran the Desclaux[8] program for $6s10d_3$, $J=1,2$ and checked $\langle r\rangle_{10d}$, $\epsilon_{10d}$, and $F^0(6s,10d)$ (direct electrostatic radial integral). These varied $<0.9\%$ for the two $J$ values. As noted in Sec. III, this assumption was essential in that is permitted us to generate a $6sns$ ($\epsilon s$) solution for $J=1$, and use it for the $J=0$ case.

Providing that the first assumption is a valid one, the types of Breit integrals $B^k$ that could appear would be of the type $B^k(6p^2;6s\epsilon l)$, where $l=s/d$. These purely valence-type integrals should be one to two orders of magnitude smaller than core valence $B^k$ integrals, and if one is going to neglect the latter (through the assumption of MCDF functions), it seems reasonable to also neglect them. The first approximation is the most difficult to justify, but some analysis has been done nonrelativistically;[25] which indicates that it is acceptable in some cases. Removal (or at least further investigation) of these two approximations will be the subject of future work (see, however, the discussion of the widths below).

To evaluate the integral in Eq. (1), an analytic fit was made[23] of the graph of each $R^k$ as a function of energy. These integrals behave quite smoothly,[23] including near the resonance positions (about which they "know" nothing), and a polynomial fit using powers smaller than 5 is quite adequate. Once the fits are made, the principal-value integral of Eq. (1) can be evaluated exactly (the off-diagonal elements are given as an explicit[16] linear combination of $R^k$ integrals. The fit also allows one to extrapolate the curves from the smallest positive energy (continuum) calculated, down to the highest ($n=16$) discrete open-channel state computed, for as is well known[26] the electrostatic $R^k$ have the (nonrelativistic) behavior,

$$n^{3/2}R^k(6p6p;6snl)\approx R^k(6p6p;6s\epsilon l) \quad \text{for } n\to\infty,\quad \epsilon\to 0\ .$$

We found the contribution from the "extrapolated region" to be quite small, no more than a few tenths of a percent. Once the shift was calculated, it could be reinserted on the right-hand side of Eq. (1) to generate an improved shift. The final converged value was no more than 4% from the initial value. The results are included in Table IV; it is interesting to note that the $J=1$ state is a "pure" $^3P$ at this level (MCDF) of approximation, so

TABLE V. Comparison of Wilson's widths with this work (eV).

| State | Channel | This work[a] | This work[b] | Wilson[c] | Expt.[d] |
|---|---|---|---|---|---|
| $^1S_0$ | $6s\epsilon s, 6sns$ | 0.298 | | 0.088 | |
| $^1D_2$ | $6s\epsilon d_{3/2}, 6snd_{3/2}$ | 0.385 | 0.395 | 0.672 | |
| | $6s\epsilon d_{5/2}, 6snd_{5/2}$ | 0.500 | 0.519 | | |
| $^3P_2$ | $6s\epsilon d_{3/2}, 6snd_{3/2}$ | 0.106 | 0.066 | 0.189 | 0.272 |
| | $6s\epsilon d_{5/2}, 6snd_{5/2}$ | 0.219 | 0.149 | | |
| $^3P_0$ | $6s\epsilon s, 6sns$ | 0.002 | | 0.007 | |

[a] Our results without correlation effects (only MCDF configurations are used for the localized portion of the resonance states).

[b] Our results with correlation effects [MCDF configurations and the configurations of $6snd$ ($6\le n\le 16$) are used for the localized portion of the resonance states].

[c] Reference 27.

[d] Reference 6.

TABLE VI. Positions of resonances (relative to $^3P_0$) in cm$^{-1}$.

| | "$^3P$"$_0$ | $^3P_1$ | "$^3P$"$_2$ | "$^1D$"$_2$ | "$^1S$"$_0$ |
|---|---|---|---|---|---|
| Expt.[a] | 90 096 | 93 980 | 96 185 | 103 232 | 109 286 |
| This work[b] | 90 096 | 94 037 | 96 508 | 105 699 | 111 051 |
| Error[c] | | 57 | 323 | 2467 | 1765 |
| Wilson[d] | 90 096 | 93 272 | 95 533 | 101 563 | 109 616 |
| Error[e] | | 708 | 652 | 1669 | 330 |

[a] References 5–7.
[b] Table IV.
[c] Absolute value of row 1 minus row 2.
[d] Reference 27.
[e] Absolute value of row 1 minus row 4.

that it should have no shift at all (at the MCDF level, $6s\epsilon s$ and $6s\epsilon d$ are incapable of forming a $^3P$). The small finite value for this shift (0.0001 eV) represents the accumulation of numerical errors made.

## VI. CALCULATION OF THE WIDTHS

The widths are calculated using Eq. (2), the "golden rule." In this work, full orthonormality is assumed (we examined the validity of this for the core spinors by looking at the $\langle 5d/5d' \rangle$ overlap integral for Hg$^+$ 6s and Hg $6p^2$. This was equal to 1.0 to within 0.05%). As for the shift, we initially made two even more stringent assumptions.

(i) We used only MCDF solutions to evaluate the integral.

(ii) We ignored the Breit operator in evaluating the matrix element.

The results we obtained using both approximations are shown in Table V (column 3), where they can be compared with Wilson's[27] results, which were obtained using a semiempirical Hartree-Fock-Slater method (scaling of the integrals). These calculations[27] included just the five configurations $6s^2+6s6d+6s7d+6s8d+6p^2$. Also listed in Table V is an experimental value for the "$^3P$"$_2$ width [the widths of other resonances are either very small ($^3P_{0,1}$) or large but not yet available ("$^1S_0$","$^1D$"$_2$)].

It can be seen that our result (Table V, column 3) is considerably larger than either Wilson's or experiment.[6] A prime candidate for the discrepancy is the failure to let $6p^2$ interact with the $6sd$ series "beyond" first order. Not only is this type of interaction, which we call[19] SEOS (symmetric exchange of symmetry) known to be a strong one, but it is just these configurations that are included in Wilson's calculation (which being CI, goes beyond first order). Our next calculation (column 4 in Table V) was done ($J=2$ states) by using *not* the MCDF solution for the localized function of Eq. (2), *but* a relativistic CI function generated by including the configurations $6p^2+6snd$. The stability of the width was studied by letting $n$ run from $n=6$ to 16. By the time the latter was reached, the width ("$^3P$"$_2$) was stable to one unit in the third nonzero digit. This corresponded to the stabilization of the $6p^2$ coefficients; we were able to directly show that one could effectively ignore contributions of the type $\langle 6snd|H|6s\epsilon d \rangle$ to the width (this was investigated by replacing $\epsilon d$ with $md$, where $m$ was large). As the $6p^2$ coefficients stabilized, they more closely approached the $LS$ limit (and hence zero width) as the $6snd$ series members were added. With $n>16$ included, the $6p$, $6p_3$ and $6p_3^2$ coefficients were 0.834 423 and 0.540 431 1. The $LS$ limits are 0.816 496 and 0.577 35.

From Table V, it can be seen that our results are generally in agreement with those of Wilson[27] and experiment,[6] where available ("$^3P$"$_2$). The greatest discrepancy occurs for the "$^1S$"$_0$ width. In this case, inclusion of the $6s^2+6s7s+6s8s$ configurations in the localized function used to calculate the width increased it only slightly; ~3% (once again, direct contributions to the width from $6s^2$,$6sns$ were ignored).

Clearly, further work on the widths should initially be in two directions: (i) use of a larger, more accurate localized function; (ii) inclusion of the Breit operator when evaluating the widths, particularly when single excitations (localized to the continuum function) are involved.

Finally, in Table VI, we compare our results for the resonance positions directly to those of Wilson[27] and experiment.[5–7] In Wilson's work[27] the position of the $^3P_0$ was adjusted to agree with the experimental position. We can see that we have accounted for the splittings within the "$^3P$" manifold better than has Wilson, but the position of the "singlets" is not as well accounted for (presuming the experimental assignments[7] have been made properly). The reasons for the differing sizes of the discrepancy are not clear at the moment—they may be connected either with the upper root nature of the "singlets," or core-valence correlation not included here.

## ACKNOWLEDGMENTS

Z.C. and D.R.B. gratefully acknowledge partial support of this work by the National Science Foundation, Grant No. 89-17746.

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