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CALCULATION OF SIEGERT EIGENVALUES FOR MOLECULAR SYSTEMS: RESULTS FOR $He(2^{1,3}S) + H$

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Abstract

The variational calculation of Siegert eigenvalues has previously been shown to provide reliable positions and widths for atomic resonances. This approach is herein extended to molecular problems, and the first such calculations for a molecular autoionizing system, $He(2^{1,3}S) + H \rightarrow He + H^+ + e^-$, are reported.

Introduction

As the authors have recently demonstrated,[1] the variational calculation of Siegert eigenvalues is a most promising approach to the determination of atomic autoionization positions and widths, in that results of useful accuracy can be obtained with quite modest basis sets. In addition, this approach is advantageous in that it involves no approximations (such as neglect of non-resonant processes, use of free particle orbitals in "golden rule" formulae, etc.) other than the finiteness of the basis set itself, it provides stable convergence to the correct result for increasing basis sets, it avoids the ambiguity of looking for "stability" of the eigenvalue as the basis set (or rotation angle, in the rotated-coordinate method) is varied, and it in principle requires little more than standard electronic

structure technology. In this letter, we extend the methods to molecular problems and present reliable results for the He(2^3S) + H and He(2^1S) + H Penning ionization systems.

Our procedure for the atomic case is briefly summarized as follows: We choose an atomic trial function ψ_t of the form

$$\psi_t(\vec{r}_1, \ldots, \vec{r}_M) = \sum_{i=1}^{N-1} c_i \Phi_i(\vec{r}_1, \ldots, \vec{r}_M) + c_N\, \Theta(\vec{r}_1, \ldots, \vec{r}_M) \quad , \qquad (1)$$

where $\{\Phi_i\}$, i = 1, ..., N-1 are bound, M-electron configurations which decay (exponentially at large distances), while Θ is an M-electron configuration involving a combination of the ground state of the (M-1)-electron system with a function which asymptotically behaves like an outgoing coulomb wave with wave vector k (the Siegert orbital). The Siegert eigenvalues are determined by requiring that the functional

$$I[\psi_t] = \int \psi_t^\dagger(\vec{r}_1, \ldots, \vec{r}_M)(H(\vec{r}_1, \ldots, \vec{r}_M) - \frac{k^2}{2})\, \psi_t(\vec{r}_1, \ldots, \vec{r}_M)\, d\vec{r}_1 \ldots d\vec{r}_M \qquad (2)$$

be stationary with respect to variation of the coefficients $\{c_i\}$. (The conjugate function $\psi_t^\dagger$ is defined by taking the complex conjugate of all spherical harmonics in ψ_t but not of the radial functions.[2]) This leads in the usual way to a secular equation for the coefficients $\{c_i\}$, which when solved yields a complex eigenvalue $E_i(k)$ which we identify on physical grounds as corresponding to the resonance. (The eigenvalue $E_i(k)$ is complex because the Hamiltonian matrix is complex symmetric, and it depends on k because the Siegert orbital does.) One then needs to choose the value of

k to satisfy the equation

$$E_i(k) - \frac{k^2}{2} = 0 \quad , \tag{3}$$

which requires iteration.

The major practical difficulty in extending this procedure to more complicated (i.e., molecular) systems lies in computing the Hamiltonian matrix elements which involve the Siegert orbital. For the autoionization of a neutral system, this function takes the form[1]

$$\Theta_{\ell m}(\vec{r}) = r^{i/k} \frac{e^{ikr}}{r} (1-e^{-r})^{\ell+2} Y_{\ell m}(\hat{r}) \quad ; \tag{4}$$

it thus has the form of a linear combination of complex Slater functions. If the bound orbitals of the basis set are chosen as Gaussian functions, the resulting matrix elements involving θ cannot be computed analytically. On the other hand, if the bound orbitals of the basis are chosen as Slater functions, <u>all</u> the molecular matrix elements cannot be computed analytically, even in the case of a diatomic system. Since numerical integration is thus unavoidable for a molecular calculation, we decided to perform our first molecular calculations on diatomic systems and employ a basis of Slater orbitals. The systems we chose to investigate are the $He(2^3S)$ + H and $He(2^1S)$ + H Penning ionization reactions. These particular systems have several desirable qualities: (1) Since they contain only three electrons, extensive electronic structure calculations are feasible. (2) Feshbach projection operator technique results are available for comparison for both systems.[3-5] (3) Sufficient experimental data exists[6-9] with which to compare

ionization cross section results obtained from the computed potentials and widths.

The main theoretical consideration in extending our procedure to molecular systems is that the problem no longer possesses spherical symmetry. In the language of a partial wave analysis, this means that Siegert orbitals of s,p,d, etc., symmetry can all contribute to the trial function, just as the bound orbitals of those symmetries do. It is important to point out, however, that the Siegert boundary condition for such a multichannel situation requires that there be only outgoing radial waves in all channels (i.e., in all partial waves in this case), so we thus include Siegert-type orbitals of s,p,d, ..., symmetry in the basis. Since the ionized electron departs primarily from the He atom in $He^* + H \rightarrow He + H^+ + e^-$, we centered the Siegert orbitals on the He center in the hope that only a few partial waves would be required to describe the resonance. This turns out to be the case.

The only remaining theoretical question is how to define the Siegert configuration. First, we note that only m = 0 Siegert orbitals need to be considered for the problems we are studying, as they possess Σ symmetry. Then for each $\theta_\ell(r)$, $\ell = 0,1,2, \ldots$, we wish to consider configurations which have the form of $\theta_\ell(r)$ times the remaining 2-electron HeH^+ core. Since the dominant configuration in ψ_{HeH^+} is $1s^2_{He} + H^+$, we take for our Siegert configurations those configurations which correspond to an orbital occupancy $\phi_a\phi_b\theta_\ell$, where ϕ_a and ϕ_b are 1s orbitals on He.

The calculations presented in this section were performed with modified versions of the HETINT and MRINO programs written by Schaefer.[10] Since all integrals were performed numerically, it was not necessary to determine

analytic expressions for the integrals involving the Siegert functions. The program was then tested in two ways: (1) the He(2^1S) resonance results obtained previously[1] were reproduced by this program; (2) setting k to a pure imaginary number (and thereby making θ_ℓ a purely real function) gave the same results as the corresponding bound calculation.

From Eq. (4), we note that the form of the Siegert function is such that the numerical integrals cannot in general be evaluated at Im(k) < 0, where Eq. (3) has the root we desire. To circumvent this problem, we first performed the calculation of $E_i(k)$ for Im(k) >> 0, fit the results to a rational fraction, and attempted to analytically continue this fitted function to the region Im(k) < 0. Unlike the atomic case,[1] however, $E_i(k)$ varied too strongly with k for this procedure to be useful. A much more successful approach was to perform the numerical integration along a rotated contour. That is, if a function f(z) is analytic in the upper half z-plane, say, then the integral $\int_0^\infty dx\, f(x)$ along the real axis is equivalent to the integral along a ray of angle α in the complex plane:

$$\int_0^\infty dx\, f(x) = \int_0^{\infty e^{i\alpha}} dz\, f(z) = e^{i\alpha} \int_0^\infty dx\, f(xe^{i\alpha}) \quad . \tag{5}$$

Since the HETINT program[10] performs the numerical integrations in ellipsoidal coordinates (ξ,η), only the ξ integrations (on the interval $[1,\infty]$) need to be performed on a rotated contour, which is defined by

$$\xi = 1 + (x-1)e^{-i\alpha} \quad ,$$

$$x = 1 \to \infty \quad . \tag{6}$$

For real values of k (which proved to be close enough to the true k for our calculations), a rotation angle $\alpha \sim 0.15\ \pi$ radians produced integrals with an error of $\lesssim 10^{-8}$ a.u. (and which are independent of the precise value of α).

The set of bound, Slater type orbitals used in the calculations presented here is the same as that used by Hickman, et al.[4] in a golden rule calculation of $He(2^3S) + H$, except that the Π orbitals are not included. The orbital basis was then augmented with Siegert functions θ_ℓ of s, p, and d symmetry centered on He. Since the change in the final Γ was less than 20% upon addition of θ_d, the inclusion of only these three Siegert orbital symmetries was considered sufficient. For the CI calculation, all $^2\Sigma$ configurations arising from the bound orbitals (240) were retained. To this set, 4 Siegert configurations were added for each Siegert orbital symmetry. These configurations have the form $\phi_a\phi_b\theta_\ell$ where ϕ_a and ϕ_b are the 1s and/or 1s' functions on He. The final CI calculation was thus performed with 252 configurations. As the real resonance energies at each internuclear separation had already been computed for our systems by the stabilization technique,[3] we could easily determine an approximate value for the real part of the true complex resonance momentum. The resonant eigenvalue $E_i(k)$ was then computed for five closely-spaced real k points bracketing this approximate value. The five resulting $E_i(k)$ values were fit to a low-order rational fraction, which was then analytically continued to the region $Im(k) < 0$ and the root Eq. (3) was found by a Newton-secant iteration.

The results for the real resonance energies as functions of the internuclear separation (i.e., the potential curves) are plotted in

Figures 1 and 2 for the singlet and triplet systems, respectively, and are compared with the results from the stabilization technique.[3,4] We see that in both cases the general agreement is quite good. Results for the singlet and triplet ionization widths as functions of R are shown in Figures 3 and 4 and compared with the golden rule results of Miller, Slocomb, and Schaefer[3] and Hickman and Morgner.[5] For the triplet case, our width agrees well with both golden rule calculations, although it seems to favor the results of Hickman, et al.[4] For the singlet system, our width is somewhat larger than Hickman's.[5] Since Hickman[5] found that to obtain good agreement between his calculated ionization cross section results and those of experiment[9] his width would have to be increased by about a factor of 2.5, and since our results are between a factor of 2 and 3 larger than Hickman's for $R \gtrsim 4\ a_o$, we feel confident that cross sections calculated from our potential and width would be in very good agreement with experiment. Such calculations are currently in progress.

Variational calculations with Siegert boundary conditions thus seem to be a practical and reliable way to carry out ab initio calculations of the energy and lifetimes of molecular autoionizing states.

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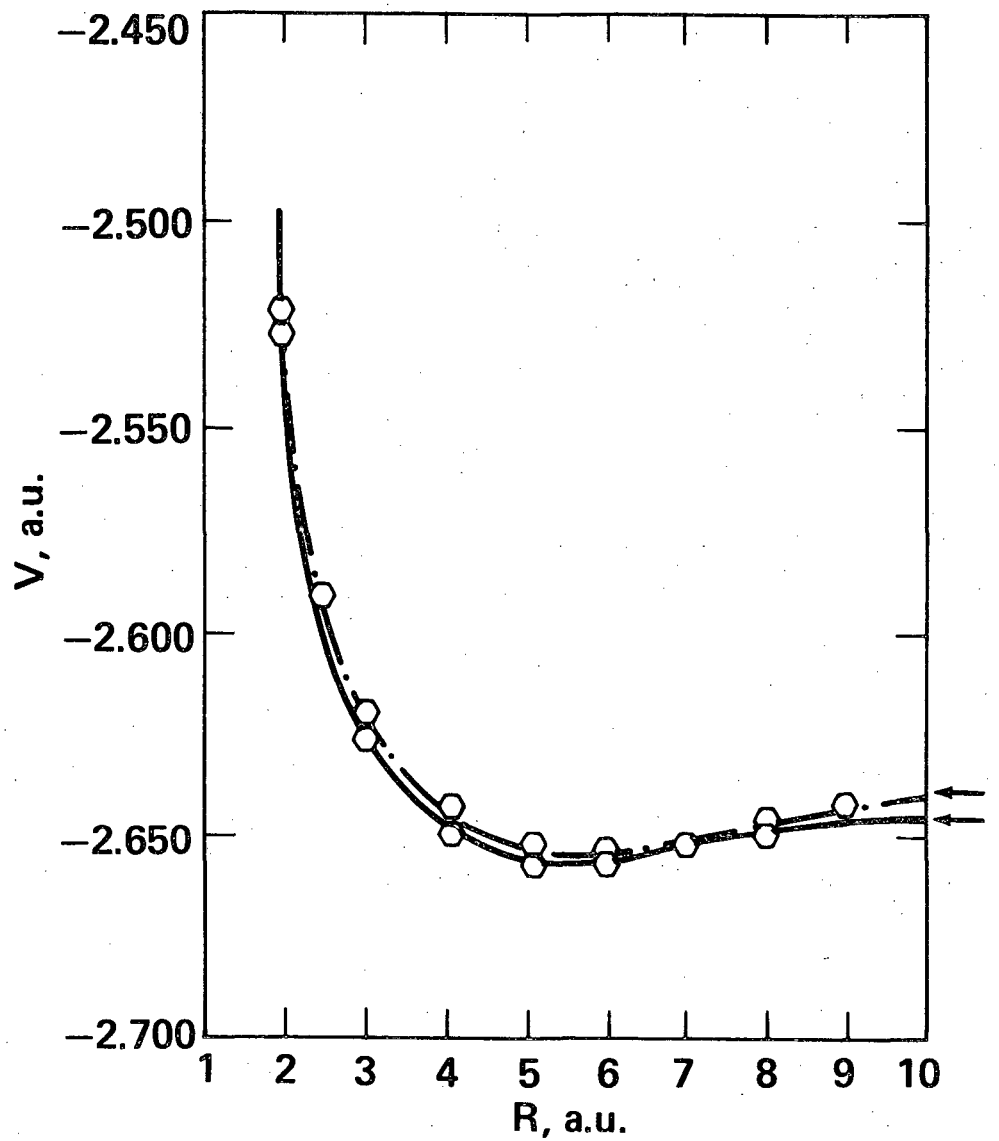
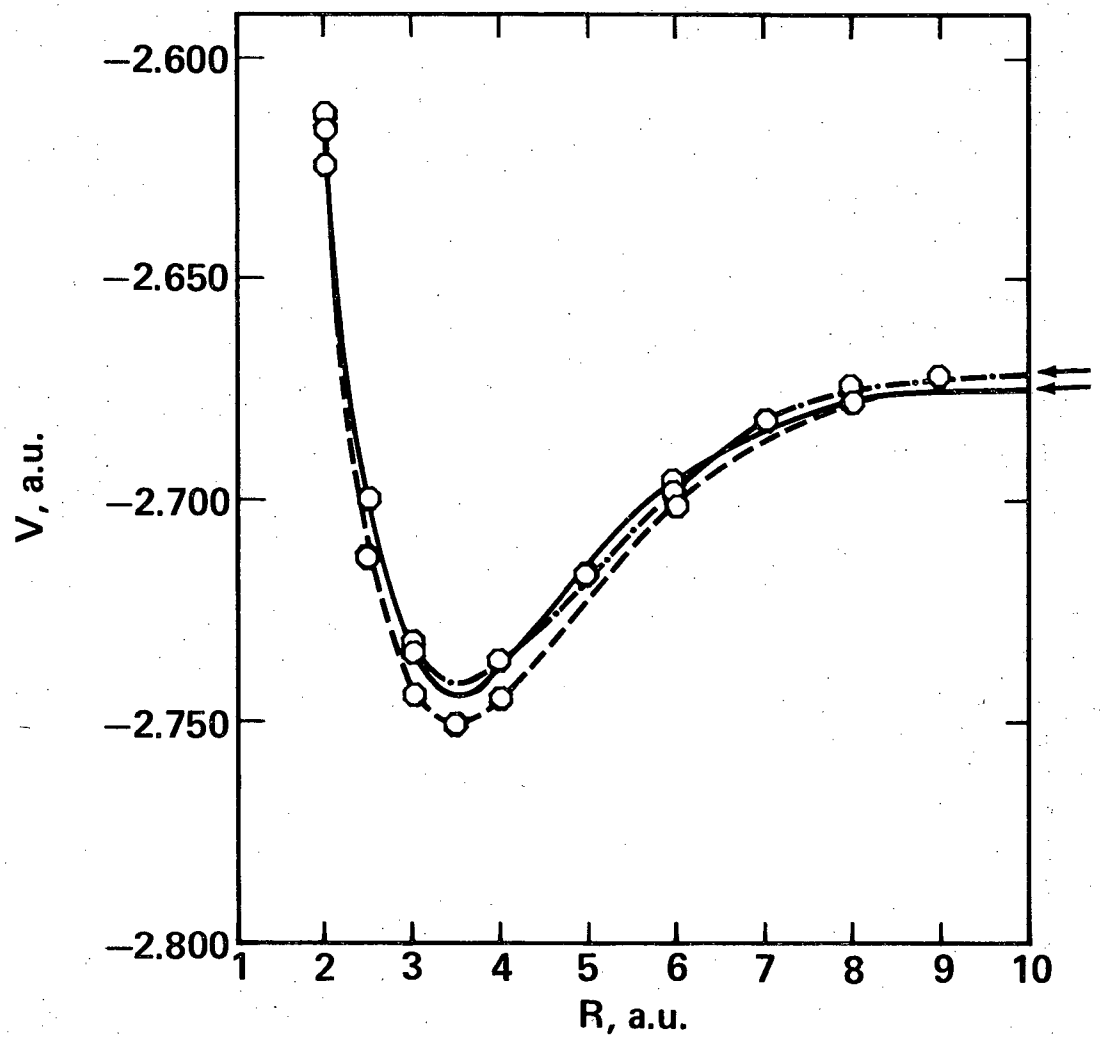
Figure Captions

1. Potential curves for He(2^1S) + H. The solid curve is the present result, obtained from the real parts of the Siegert eigenvalues for various values of R. The dashed curve was obtained by the stabilization method (see Reference 3). The corresponding asymptotic limits are indicated by arrows.
2. Potential curves for He(2^3S) + H. The solid curve is the present result, obtained from the real parts of the Siegert eigenvalues for various values of R. The other curves were obtained by the stabilization method. The dashed curve was taken from Reference 4, while the dot-dashed curve was taken from Reference 3. The corresponding asymptotic limits are indicated by arrows.
3. Autoionization widths Γ for He(2^1S) + H. The solid curve is the present result, obtained from the imaginary parts of the Siegert eigenvalues for various values of R. The dashed curve was obtained by the golden rule method (see Reference 5). The dashed extension of the solid curve is an assumed result, as the imaginary part of the Siegert eigenvalues for R = 8 a_o was below the limit of accuracy for the calculation.
4. Autoionization widths Γ for He(2^3S) + H. The solid curve is the present result, obtained from the imaginary parts of the Siegert eigenvalues for various values of R. The other curves were obtained by the golden rule method. The dashed curve was taken from Reference 5, while the dot-dashed curve was taken from Reference 3.



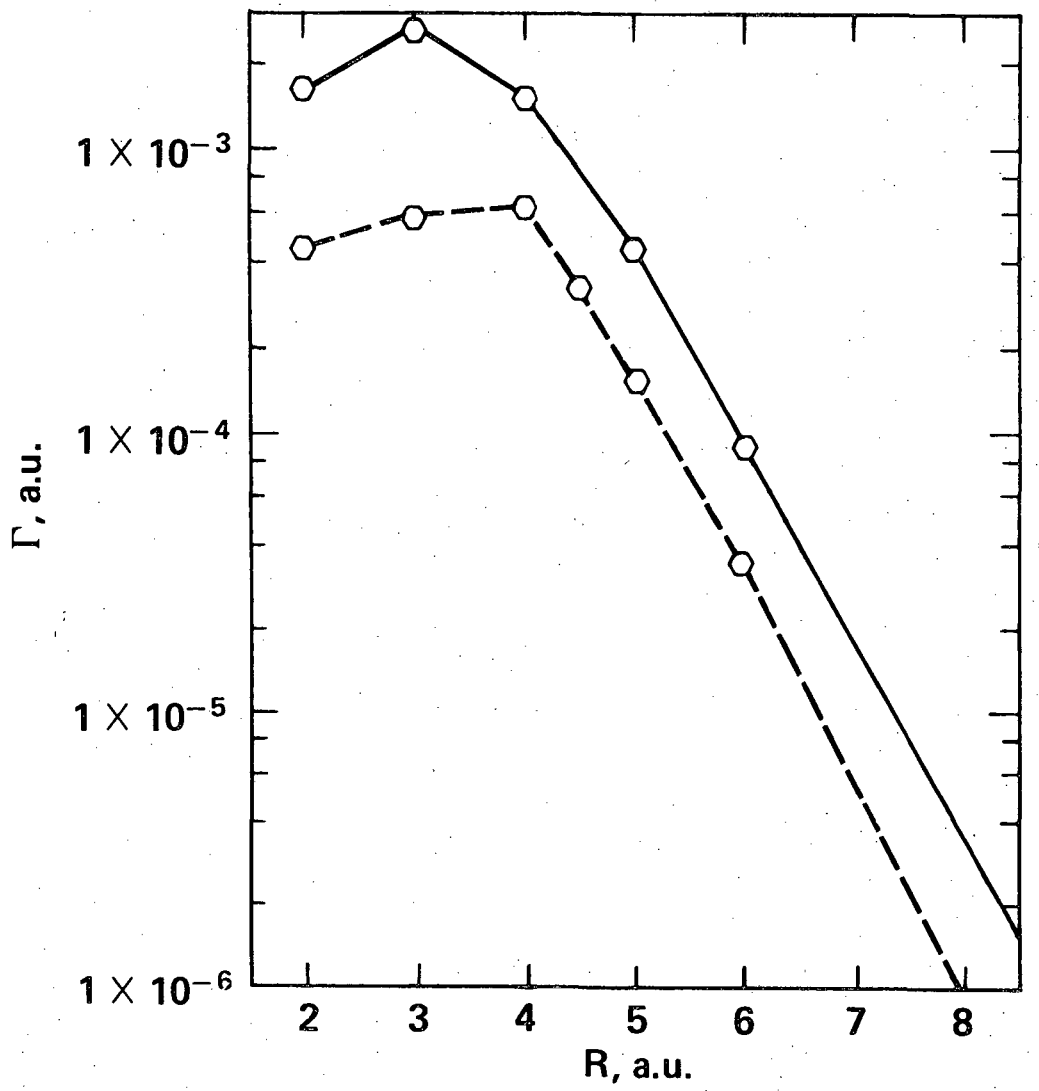
XBL 788-10360

Figure 1.



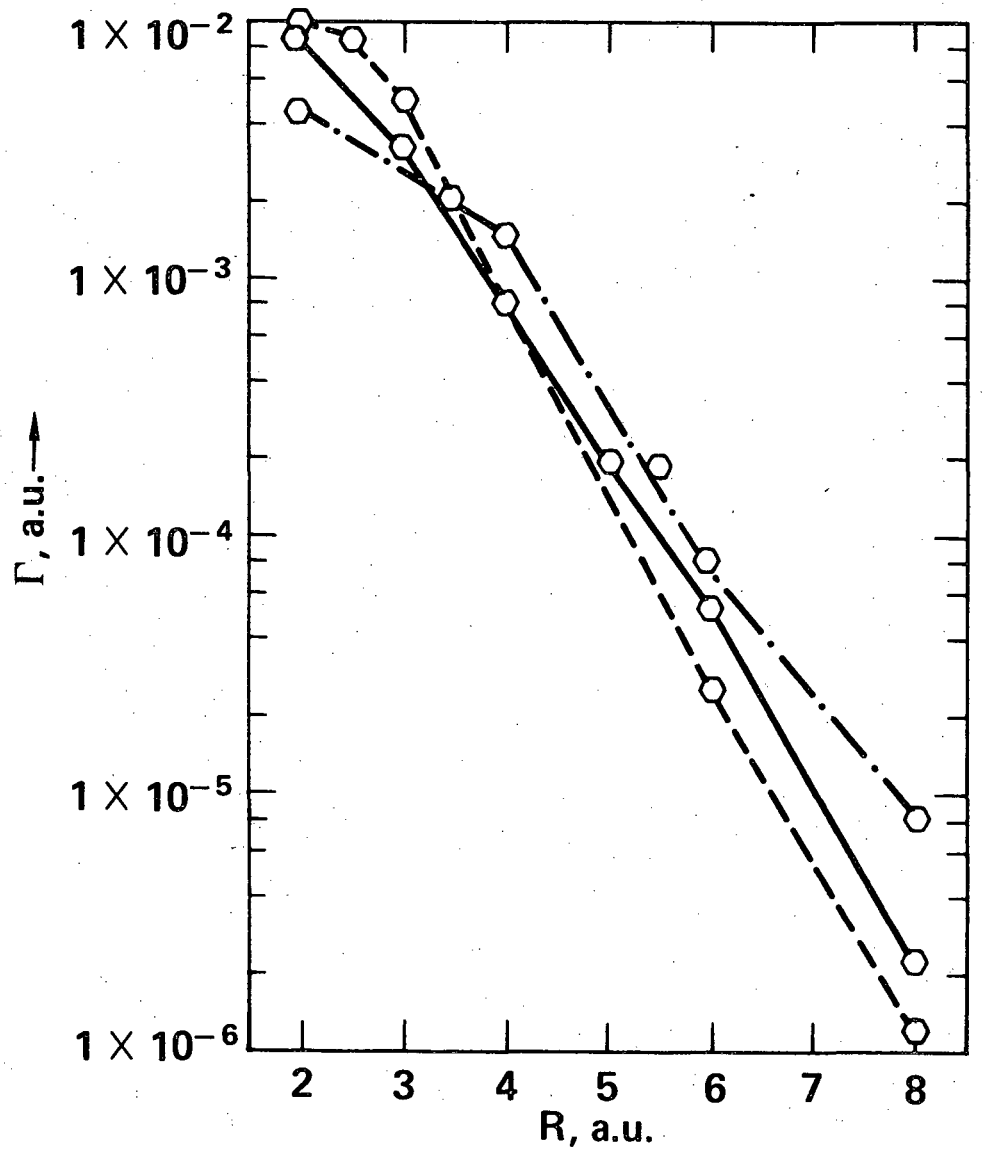
XBL 788-10361

Figure 2.



XBL 788-10359

Figure 3.



XBL 788-10358

Figure 4.

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