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LIFETIMES FOR $\text{He}(2^3\text{S})\text{-H}$ AND $\text{He}(2^3\text{S})\text{-H}_2$

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Feshbach Projection Operator Calculation of the Potential Energy
Surfaces and Autoionization Lifetimes for $\text{He}(2^3\text{S})\text{-H}$ and $\text{He}(2^3\text{S})\text{-H}_2^*$

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Abstract

A new technique has been developed for calculating potential energy surfaces and widths for autoionizing molecular systems. The method is based on the use of the Feshbach projection operators P and Q , which are defined within the space of configurations generated from a basis set of square-integrable orbitals. Autoionizing states are then obtained by diagonalizing a particular subblock of the finite Hamiltonian constructed by the CI procedure. These states decay because they are only approximate eigenfunctions of the full finite Hamiltonian. Their lifetimes are evaluated using continuum functions which are expanded in the basis orbitals. Such an expansion is shown to be sufficiently accurate. The present technique is compared with the stabilization method and is found to illuminate certain features of that procedure. Potential surfaces V^* and widths Γ have been calculated for the Penning ionization transitions $\text{He}(2^3\text{S}) + \text{H} \rightarrow \text{He} + \text{H}^+ + \text{e}^-$ and $\text{He}(2^3\text{S}) + \text{H}_2 \rightarrow \text{He} + \text{H}_2^+ + \text{e}^-$.

I. INTRODUCTION

A "first principles" treatment of collisional ionization phenomena within the Born-Oppenheimer approximation requires calculation of the potential energy curves (or surfaces) and the lifetime, or width, for autoionization of the molecular system. Penning ionization of an atom or molecule by a metastable helium atom,

is an important example of this type of process. Within a classical or semi-classical theory, essentially all aspects of the collision dynamics of reaction (1)--the ionization cross sections, the relative amounts of atomic (X^+) and molecular (HeX^+) ions, and the energy distribution of the ionized electrons--are determined by the three functions V^* , V_+ , and Γ . V^* and V_+ are the potential energy surfaces (that is, electronic energies as functions of nuclear positions) for He^*-X and $\text{He}-\text{X}^+$, respectively, and $\Gamma/\hbar$ is the autoionization rate as a function of nuclear coordinates. (Alternately, $\hbar/\Gamma$ is the lifetime of the He^*X state with respect to autoionization). Somewhat more detailed information is required for a completely quantum mechanical calculation; this has been discussed by Miller,¹ Nakamura,² and Hickman and Morgner.³

Since V_+ is the electronic energy for an ordinary bound electronic state of HeX^+ , it can be obtained using the standard techniques of electronic structure calculation (e.g., Hartree-Fock or configuration interaction (CI)). It is a less straightforward matter to obtain V^*

and Γ , because the discrete electronic energy V^* is embedded in a continuum of electronic states. However, a variety of techniques has been developed for dealing with this situation.

In 1970 Miller and Schaefer⁴ carried out an elaborate calculation of V^* for the $\text{He}(2^3\text{S})\text{-H}$ system using the stabilization method.⁵⁻⁷ Γ was obtained for the same system in 1972 by Miller, Slocumb, and Schaefer⁸ (MSS) using the Golden Rule approximation of Miller.⁹ The specific methods employed in this calculation, however, were limited to diatomic molecules because of the use of continuum orbitals. The only other calculation recently reported for a Penning ionization system was performed by Cohen and Lane¹⁰ for $\text{He}(2^{1,3}\text{S})\text{-H}_2$. The applicability of their technique was somewhat limited because a single-center expansion was used to describe the H_2 molecule. Cohen and Lane¹⁰ obtained results only for the equilibrium bond length of H_2 . In the present paper we describe a somewhat different approach to the problem of calculation V^* and Γ . The method can be efficiently applied to polyatomic systems, and does not require the evaluation of Hamiltonian matrix elements between bound and continuum configurations. Results are obtained for the systems $\text{He}(2^3\text{S})\text{-H}$ and $\text{He}(2^3\text{S})\text{-H}_2$.

Section II describes the formalism and method of calculation, which are essentially a direct application of the Feshbach projection operator approach.^{11,12} The key feature of this procedure is the discovery of a practical way to define the projection operators P and Q which appear in the theory. The other feature which is important in making the overall approach applicable to polyatomic systems is that standard CI computational techniques can be applied with very little modification. This is possible

because of the discovery that the continuum orbitals which appear in the matrix elements needed to calculate Γ can be accurately expanded as linear combinations of the discrete molecular orbitals.

In Section III this new approach is applied to $\text{He}(2^3\text{S})-\text{H}$. The results are discussed and compared with the earlier work of MSS. The principal new results, those for $\text{He}(2^3\text{S})-\text{H}_2$, are presented and discussed in Section IV. Section V contains concluding remarks.

II. THEORY

A. Preliminary Discussion

In the discussion below, we will specialize the notation to the system $\text{He}(2^3\text{S})-\text{H}$, which can autoionize to $\text{HeH}^+ + e^-$. This process is an example of Penning ionization and occurs during a collision of He^* and H . Within the Born-Oppenheimer approximation, however, one first solves the electronic problem for fixed nuclei, which in this case is a problem of molecular autoionization. Having solved the electronic problem for fixed nuclei and obtained the electronic energy and autoionization rate of He^*-H , one may then calculate various aspects of the collision dynamics.

Let H be the electronic Hamiltonian (the coordinate R , the internuclear separation, is suppressed). The appropriate eigenfunctions of H have two essentially different components.¹³ One resembles a bound state and decays asymptotically. As $R \rightarrow \infty$, this component separates to $\text{He}(2^3\text{S})$ and H . The other component resembles an HeH^+ core and a function which asymptotically becomes a Coulomb wave. We assume that one chooses an orthonormal set of square integrable (spatial) orbitals $\{\phi_1, \dots, \phi_n\}$ flexible enough to represent both components of an eigenfunction within a finite region of space. Then the configurations Φ are constructed as linear combinations of Slater determinants of these orbitals which have the desired molecular symmetry. We shall write Slater determinants as $|\phi_i(\vec{r}_1)\overline{\phi_j(\vec{r}_2)}\phi_k(\vec{r}_3)|$; an overbar designates spin down. The set of orthonormal configurations $\{\Phi_i\}_{i=1, \dots, N}$ is a basis for the space $\hat{A}$ of three electron wave functions. $\hat{A}$ is a subspace of A , which is the space of all possible three electron wave functions.

We denote by $\hat{H}$ the operator obtained by truncating H to the space $\hat{A}$. Thus

$$\hat{H} = \sum_{i,j=1}^N |\phi_i\rangle H_{ij} \langle \phi_j| \quad (1)$$

where

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \quad (2)$$

Finally, let ψ_{HeH^+} denote a wave function for the ground state of HeH^+ constructed from the orbitals $\{\phi_1, \dots, \phi_n\}$. ψ_{HeH^+} is therefore an approximation to the ground state of the system with one less electron.

B. Formalism

It is known that certain eigensolutions of H in the space A are characterized by the mixing of bound- and continuum-like components.¹³ We wish now to partition $\hat{A}$ in a way which allows us to identify two components of the corresponding eigenfunctions of $\hat{H}$ in an analogous manner. To do this we define

$$\chi_i^0 = A \psi_{\text{HeH}^+}(\vec{r}_1, \vec{r}_2) \phi_i(\vec{r}_3) \quad i = 1, \dots, n \quad (3)$$

where A is the antisymmetrizer. Clearly each χ_i^0 has the physical form of an ionic core plus another orbital and can be written as a linear combination of the $\{\phi_i\}$. The set $\{\chi_i^0\}$ spans a subspace of $\hat{A}$. In order to define a projector onto this subspace, it may be necessary to orthonormalize the χ_i^0 . Let this new set of elements of $\hat{A}$ be $\{\chi_i\}$. Then

$$P = \sum_{i=1}^n |\chi_i\rangle \langle \chi_i| \quad (4)$$

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and

$$Q = 1 - P \quad (5)$$

are the desired projection operators. The physical content of the definition is that any element in the P subspace of $\hat{A}$ may be written as an antisymmetric product of ψ_{HeH^+} and another function $f(\vec{r}_3)$.

We now summarize the essential results of Feshbach's analysis.^{11,12} An autoionizing state (or resonance) occurs at energy $E_r + \Delta$, where E_r is an eigenvalue of QHQ with eigenvector ψ_r and the small shift Δ is usually neglected. The lifetime of the autoionizing state (or the width of the resonance) is (in atomic units)

$$\Gamma = 2\pi\rho |\langle P\chi | PHQ | \psi_r \rangle|^2 \quad (6)$$

ρ , the density of states, is related to the asymptotic normalization of $P\chi$, which satisfies

$$(PHP + \Delta H - E_r) P\chi = 0 \quad (7)$$

where

$$\Delta H = \sum_j' \frac{PHQ|\psi_j\rangle\langle\psi_j|QHP}{E_r - E_j} \quad (8)$$

The primed sum runs over all eigenvalues E_j and eigenvectors ψ_j of QHQ except for $j = r$.

At this point we make a physical assumption about the form of $P\chi$. As in previous work,⁸ we make a partial wave expansion and assume

$$P\chi_\ell = A \psi_{\text{HeH}^+}(\vec{r}_1, \vec{r}_2) \frac{1}{r_3} F_\ell(-1/k, kr_3) Y_{\ell 0}(\hat{r}_3) \quad (9)$$

where F_ℓ is the radial Coulomb wave function and $k^2/2$ is the energy of the ionized electron in atomic units. F_ℓ is centered on H^+ (or on the midpoint of H_2^+) and has the asymptotic form $\sin[kr + (1/k)\ln 2kr - \pi\ell/2 + \sigma_\ell]$ so that $2\pi\rho = 4/k$; $\sigma_\ell = \arg \Gamma(\ell+1 - i/k)$ is the usual Coulomb phase shift. Then it can be shown⁸

$$\Gamma = 2\pi\rho \sum_{\ell=0}^{\infty} |\langle P\chi_\ell | PHQ | \psi_r \rangle|^2 \quad (10)$$

We denote the continuum orbital $\frac{1}{r} F_\ell Y_{\ell 0}$ by $\phi_c^{(\ell)}$. Then $\phi_c^{(\ell)}$ may be expanded in terms of the orbitals $\{\phi_1, \dots, \phi_n\}$:

$$\phi_c^{(\ell)} = \sum_{i=1}^n \alpha_i^{(\ell)} \phi_i + \tilde{\phi}_c^{(\ell)} \quad (11)$$

where

$$\alpha_i^{(\ell)} = \langle \phi_i | \phi_c^{(\ell)} \rangle \quad (12)$$

and $\tilde{\phi}_c^{(\ell)}$ is effectively defined by Eq. 11. Our calculations have shown that for our P and Q, $\tilde{\phi}_c^{(\ell)}$ may be neglected. Since this is the part of $\phi_c^{(\ell)}$ which is not square integrable, a great simplification is achieved by writing

$$P\chi_\ell = A \psi_{\text{HeH}^+}(\vec{r}_1, \vec{r}_2) \phi_c^{(\ell)}(\vec{r}_3) \quad (13)$$

$$\approx A \psi_{\text{HeH}^+}(\vec{r}_1, \vec{r}_2) \left(\sum_{i=1}^n \alpha_i^{(\ell)} \phi_i(\vec{r}_3) \right) \quad (14)$$

This approximation to $P\chi_\ell$ is an element of $\hat{A}$, and thus Γ may be written in terms of the matrix elements H_{ij} already calculated.

C. Physical Interpretation

The autoionization of the "bound state" $\text{He}(2^3\text{S})\text{-H}$ and electron scattering by HeH^+ are described by the same electronic Hamiltonian. A very simple physical interpretation of the relation between these two phenomena is possible within our formalism. It is only necessary to perform an orthogonal transformation on the orbitals $\{\phi_1, \dots, \phi_n\}$ such that the new ϕ_1 is a Self-Consistent Field (SCF) 1σ orbital of HeH^+ . This may be done routinely with various electronic structure codes¹⁴ to obtain

$$\psi_{\text{HeH}^+} \approx |\phi_1(\vec{r}_1)\phi_1(\vec{r}_2)| \quad (15)$$

Then the following configurations are basis vectors of the P subspace of $\hat{A}$:

$$\chi_i \approx |\phi_1(\vec{r}_1)\phi_1(\vec{r}_2)\phi_i(\vec{r}_3)|, \quad i = 2, 3, \dots, n \quad (16)$$

All other configurations lie in the Q subspace of $\hat{A}$. This explicitly shows that each χ_i has the physical form of an ionic HeH^+ core, plus another orbital.

One then orders the configurations ϕ_i such that those spanning the Q subspace precede those spanning the P subspace. Then the matrix of $\hat{H}$ blocks:

$$\begin{bmatrix} Q\hat{H}Q & Q\hat{H}P \\ P\hat{H}Q & P\hat{H}P \end{bmatrix} \quad (17)$$

An explicit representation of $\hat{H}$ is thereby obtained. It is an example of the quasiadiabatic representation of H discussed formally by O'Malley.¹⁵ Autoionizing states are found by diagonalizing $Q\hat{H}Q$. These states are only approximate eigenfunctions of $\hat{H}$; autoionization occurs because of the off diagonal elements $P\hat{H}Q$. Of course, since $\hat{H}$ has only a finite number of eigenstates, the final "continuum state" $P\chi_\ell$ must be constructed by hand. $P\hat{H}P$ may also be diagonalized. Since solutions to this subblock of $\hat{H}$ have the form $A \psi_{\text{HeH}^+}(\vec{r}_1, \vec{r}_2) f(\vec{r}_3)$, $P\hat{H}P$ may be identified as a representation of the static-exchange Hamiltonian for $e^- - \text{HeH}^+$ scattering.

We have claimed (and will subsequently demonstrate) that the neglect of $\tilde{\phi}_c^{(\ell)}$ is justified. The physical reasoning behind this assumption is as follows. If $\{\phi_1, \dots, \phi_n\}$ is a good basis within a localized region of space, then $\sum_{i=1}^n \alpha_i^{(\ell)} \phi_i$ should be a good approximation to $\phi_c^{(\ell)}$ in this region, and so $\tilde{\phi}_c^{(\ell)}$ will only be large outside this region. However, the dominant contribution to the width integrals (Eq. 10) will come from the region of space where ψ_r is large, the "inner" region. Hence truncating the continuum orbital to this "inner" region does not cause a significant loss of accuracy in the width.

D. Alternate Definitions of P and Q

Other definitions of P and Q are permitted by the formalism. The only limitation is that

$$\lim_{r_1 \rightarrow \infty} P\Psi = \Psi \quad (18)$$

where Ψ is the full electronic eigenfunction of H . Many calculations have employed the stabilization method,⁵⁻⁷ which divides physical space

into an "inner" and "outer" region. Thus Q_s ($=Q_{\text{stabilization}}$) projects onto the entire space $\hat{A}$, and $Q_s H Q_s = \hat{H}$. P_s is not defined within $\hat{A}$, only within the larger space A (of functions which may be large in the "outer" region of space). The difference between these two possible definitions of the projection operators may be simply illustrated. Consider the approximation to $P\chi_\ell$ introduced in Eq. 14; this is a "truncated continuum function." Using the present definition, this function is an element of the P subspace of $\hat{A}$ because it has an ionic core. Alternatively, it could be considered an element of the Q_s subspace of Q because it decays asymptotically in the "outer" region of physical space.

The appearance of "stable roots" as the basis set is enlarged is a characteristic feature of the stabilization method. In our calculations we observed that the eigenvalues of $\hat{H}$ are almost exactly the same as those of $\hat{Q}\hat{H}\hat{Q}$ and those of $\hat{P}\hat{H}\hat{P}$. This is because the off diagonal elements of $\hat{P}\hat{H}\hat{Q}$ are very small. Furthermore, as the basis is enlarged, the eigenvalues of $\hat{P}\hat{H}\hat{P}$ change, and those of $\hat{Q}\hat{H}\hat{Q}$ remain stable. The difference is that if one diagonalizes $\hat{H}$ without first constructing the subblocks, the eigenvalues are interspersed.

This has two consequences, one aesthetic and one practical. First, it is appealing that all the eigenvalues of $\hat{Q}\hat{H}\hat{Q}$ correspond to true "resonance" states which can autoionize to $\text{HeH}^+ + e^-$. The ground state of HeH is obtained as one of the eigenvalues of $Q_s H Q_s = \hat{H}$. Secondly, in the calculations on $\text{He}(2^3\text{S})-\text{H}$, it was found that the desired eigenvalue was the lowest root of $\hat{Q}\hat{H}\hat{Q}$. The lowest eigenvalue of a matrix can generally be extracted more quickly and easily than the higher roots.

We may now briefly survey other definitions of the projection operators which have been proposed. For two electron atoms, O'Malley and Geltman¹² as well as Bhatia and Tempkin¹⁶ define

$$Q = \prod_{i=1}^2 \left(1 - |\phi_{1s}(\vec{r}_i)\rangle\langle\phi_{1s}(\vec{r}_i)| \right) \quad (19)$$

$$P = 1 - Q \quad (20)$$

where ϕ_{1s} is the exact hydrogenic ground state for the one electron system. This definition was generalized to N electron systems by O'Malley.¹⁷ He wrote

$$Q = \prod_{i=1}^N \left(1 - |\phi_{N-1}(\vec{r}_i)\rangle\langle\phi_{N-1}(\vec{r}_i)| \right) \quad (21)$$

$$= \prod_{i=1}^N (1 - P_i) \quad (22)$$

$$P = 1 - Q \quad (23)$$

where $\phi_{N-1}(\vec{r}_i)$ is the ground state of the N-1 electron system written as a function of all the coordinates $\vec{r}_1, \dots, \vec{r}_N$ except $\vec{r}_i$. Within any particular finite dimensional space $\hat{A}$, this definition is equivalent to ours. Temkin, Bhatia, and Bardsley¹⁸ considered approximations to Eq. 22 obtained by neglecting the cross terms $P_i P_j$. In their formulation the idempotency requirement ($Q^2 = Q$) is relaxed, but Eq. 18 is still satisfied. Finally, Lippmann and O'Malley¹⁹ have observed that since E_r and Δ depend on P and Q (although $E_r + \Delta$ does not), one should choose P and Q such that $\Delta = 0$. These last two methods, however, have not yet been applied to molecular systems.

III. $\text{He}(2^3\text{S})-\text{H}$

The autoionization width $\Gamma(R)$ for the transition $\text{He}(2^3\text{S})-\text{H} \rightarrow \text{He} + \text{H}^+ + e^-$ has been calculated using several different approximations:

1. We reproduced the previous calculation of Miller, Slocumb, and Schaefer⁸ (MSS), with certain simplifying assumptions. The method employed by MSS differs from the procedure described in this paper, and somewhat different results are obtained. These differences will be discussed.
2. We evaluated $\Gamma(R)$ according to Eqs. 10 and 13, including $\tilde{\phi}_c^{(\ell)}$. This and the previous calculation required the numerical calculation of Hamiltonian matrix elements between bound and continuum configurations.
3. We evaluated $\Gamma(R)$ from Eqs. 10 and 14. This demonstrated that the effect of neglecting the asymptotic part of $\phi_c^{(\ell)}$ was indeed small.
4. Our final results were obtained using a different (and somewhat larger) basis to repeat the third set of calculations. Γ was thereby shown to be only weakly dependent on the basis set.

For the first three calculations we used the first basis listed in Table I. This basis is the same as that used by MSS, except that π orbitals are not included. This reduced the number of possible three electron configurations (of a full CI for $^2\Sigma$ symmetry) from 321 to 240. Also, MSS used a 51 configuration wave function for HeH^+ . In the present work we used a single determinant SCF wave function constructed from the basis orbitals.

Calculation (1) was performed using the following formulas from MSS:

$$\Gamma = 2\pi\rho \sum_{\ell} |I_{\ell}'|^2 \quad (24)$$

$$I_{\ell}' = \langle P\chi_{\ell}' | H - E_r | \psi_r' \rangle \quad (25)$$

$$P\chi_{\ell}' = A \psi_{\text{HeH}^+}(\vec{r}_1, \vec{r}_2) \tilde{\phi}_c^{(\ell)}(\vec{r}_3) \quad (26)$$

ψ_{HeH^+} is the SCF determinant and ψ_r' is the entire 240 configuration eigenvector of $\hat{H}$. For this choice of ψ_r' , only the $\tilde{\phi}_c^{(\ell)}$ part of $\phi_c^{(\ell)}$ contributes to I_{ℓ}' .⁴ Thus the calculation of bound-continuum matrix elements cannot be avoided. As expected, the results of this calculation were very similar to those of MSS. Most partial widths I_{ℓ} changed less than 10%; $\Gamma(R)$ changed by about 20% at $R = 2, 4$, and $8 a_0$. This served as a check of our programming and provided some justification that the SCF approximation to ψ_{HeH^+} is not too severe.

For calculations (2) and (3), ψ_r is the 232 configuration eigenvector of $\hat{QH}Q$ defined by Eq. 17, and the appropriate formulas are

$$\Gamma = 2\pi\rho \sum_{\ell} |I_{\ell}|^2 \quad (27)$$

$$I_{\ell} = \langle P\chi_{\ell} | H | \psi_r \rangle \quad (28)$$

$$P\chi_{\ell} = \sum_{i=2}^9 \alpha_i^{(\ell)} |\phi_1(\vec{r}_1)\phi_1(\vec{r}_2)\phi_1(\vec{r}_3)| \\ + |\phi_1(\vec{r}_1)\phi_1(\vec{r}_2)\tilde{\phi}_c^{(\ell)}(\vec{r}_3)| \quad (29)$$

In calculation (2) the full form of $P\chi_{\ell}$ was used. In calculation (3) the term involving $\tilde{\phi}_c^{(\ell)}$ was neglected, and hence Γ could be written

entirely in terms of the expansion coefficients $\alpha_i^{(l)}$ (Eq. 13) and the matrix elements $\hat{P}HQ$ (Eq. 17). Tables 2 and 3 summarize the results of these calculations. Generally speaking, for a given R , the larger I_ℓ are more accurate in the truncated calculation than the smaller I_ℓ . However, the quantity of interest, Γ , is determined mainly by the larger I_ℓ . The difference in $\Gamma(R)$ between calculations (2) and (3) is only 4% at $R = 2 a_0$ and $4 a_0$ and 16% at $R = 8 a_0$.

For calculation (4) we used the second basis set given in Table 1. To check the sensitivity to orbital exponents, we have varied slightly those used by MSS. Nearly a full CI was done; all possible configurations using three σ orbitals, and all double excitations into π orbitals from the reference state $1\sigma^2 2\sigma$ were included. (Recall that the 1σ orbital is obtained from HeH^+). Tables 4 and 5 list the results obtained. The values for Γ changed about 10% at $R = 6 a_0$ and $8 a_0$, where both basis sets gave nearly the same electronic energy. For smaller R , the resonance energy changed somewhat, and Γ changed by about 25%. The calculated well depth D for V^* , the $\text{He}(2^3\text{S})\text{-H}$ potential, was 2.07 eV, compared with a value $D = 1.91$ eV obtained by MSS. The present result is thus in slightly better agreement with the value $D = 2.31 - 2.36$ eV determined by Morgner²⁰ by fitting Penning electron energy distributions, but not significantly so.

At each value of R , the energy of the ejected electron is given by the difference in the electronic energies of the resonance state and the molecular ion HeH^+ . For the latter energy we used the recent calculation of Kołos and Peek.²¹ The energy difference $\epsilon = \frac{1}{2} k^2$ (a.u.) determines the wave number k of the coulomb orbital used to evaluate Eqs. 27-29, and also the factor $2\pi\rho = 4/k$. We have tested the sensitivity of the width to k , which corresponds

to calculating the "off-shell" matrix elements $V_{\epsilon\lambda}(R)$ discussed by Hickman and Morgner.³ The trend is clear. A 10% increase (decrease) in k causes roughly a 20% decrease (increase) in $\Gamma(R)$.

Calculations (1) and (4) give somewhat different results. For the real part of the potential surface, $V^*(R)$, the small difference is merely a matter of the choice of basis set. For $\Gamma(R)$, the discrepancy is larger, especially in the asymptotic region, as shown in Figure 1. It is thought that the reason for this difference is more subtle than simple basis set dependency. This is because the results using two different basis sets (calculations (3) and (4)) differ by only 10-25%, whereas calculations (1) and (4) disagree by nearly an order of magnitude at $R = 8 a_0$. Unfortunately, experimentally measurable quantities are not sensitive to the asymptotic form of $\Gamma(R)$, because $V^*(R)$ is attractive. If $V^*(R)$ were repulsive, it would be very easy to distinguish between the two widths by examining the energy dependence of the ionization cross section. For systems where $V^*(R)$ is repulsive (such as $\text{He}(2^3\text{S})\text{-Ar}$ or $\text{He}(2^3\text{S})\text{-H}_2$), it can be very important to calculate the asymptotic part of $\Gamma(R)$ correctly.

The primary difference between calculation (1) and the other three is the choice of the projectors P and Q . MSS takes ψ_r' to be the eigenvector of $Q_S H Q_S = \hat{H}$. This is the most convenient definition of Q because the matrix H need not be partitioned, but the physical meaning of $P = 1-Q$ is unclear. This increases the practical difficulty of solving Eq. 7, and the accuracy of the approximate solution assumed Eq.(9 or 26) is not easily assessed. In the present formulation, however, we begin by defining the P projector in a convenient and physically reasonable way. Then $Q = 1-P$ is more complicated but still easily handled. The exact solution $P\chi$ to Eq. 7 is

still difficult to obtain. Neglecting ΔH , the function $P\chi$ is the solution of the static-exchange Hamiltonian $P\hat{H}P$. It is possible to solve the static-exchange problem numerically with present day methodology, but this is of course more involved. Our $P\chi$ seems to be a reasonable zeroth-order solution to the static exchange Hamiltonian $P\hat{H}P$. If a better solution were obtained, our results suggest that it could be projected onto the basis $\{\phi_1, \dots, \phi_n\}$ without significant loss of accuracy.

IV. $\text{He}(2^3\text{S})-\text{H}_2$

A. Computational Details

The calculation of the matrix elements of the electronic Hamiltonian was performed using the Gaussian 70 SCF program plus the CI package developed by Morokuma and coworkers. To facilitate identification of the proper eigenvector of H_{QQ} , we used a basis of Slater-type-orbitals (STO-s) as shown in Table 6. Each STO was expanded in six Gaussian orbitals. Several comments may be made about the choice of basis. It is necessary to describe accurately both the resonance $\text{He}(2^3\text{S})-\text{H}_2$ state and the ionic HeH_2^+ state. The use of double-zeta-plus-polarization orbitals on each H is clearly sufficiently flexible to do this. For the He orbitals, we optimized the exponent of the 2s function in a separate calculation on $\text{He}(2^3\text{S})$.

From the point of view of standard electronic structure techniques, our choice of HeH_2^+ molecular orbitals to describe the $\text{He}(2^3\text{S})-\text{H}_2$ state is somewhat unconventional. This choice is made to simplify the definition and use of the Feshbach projection operators; we have performed various tests which indicate that the accuracy of the potential surface obtained is not diminished. It is well known that if a full CI is done, the eigenvalues of the CI Hamiltonian do not change when the basis orbitals are "rotated" by an orthogonal transformation. We therefore performed trial calculations with a basis set sufficiently small that a full CI could be done. (That is, every possible symmetry allowed configuration was retained). This basis was obtained by deleting the three p orbitals on each H. We then compared the potential curves obtained for $\text{He}(2^3\text{S})-\text{H}_2$ by doing a full CI, and by keeping only single and double excitations from the reference occupancy $\phi_1\phi_1\phi_2\phi_2$. ϕ_1 and ϕ_2 were the orbitals obtained in the SCF calculation of

$\psi_{\text{HeH}_2^+} = |\phi_1 \bar{\phi}_1 \phi_2|$. The two potential curves obtained were virtually identical (after correcting for different asymptotic limits). Furthermore, the widths calculated using the two different ψ_r s differed by less than 5%. Hence in our final calculations with the full basis we included only single and double excitations. This gave a modest number of configurations for the diagonalization of H_{QQ} : 150 for the C_{2v} geometries, 237 for $C_{\infty v}$, and 315 for C_s . It was found that the curve obtained with the larger basis was less repulsive than the "trial" curve, although this effect was less pronounced for the collinear ($C_{\infty v}$) geometry.

The only other computational techniques to be mentioned concern the overlap integrals between the Coulomb orbitals and the basis functions. The Coulomb orbitals were evaluated using the continued fraction algorithm of Steed,²² and the integrals were done by Gaussian quadrature.

B. Results and Discussion

We have checked the results of our structure calculation in two asymptotic limits. We found that if the $\text{He}(2^3\text{S})$ was far removed, and the H_2 bond length varied, that the energy dependence was just that of an isolated H_2 . In this case the dominant configuration was approximately $1s_{\text{He}} 2s_{\text{He}} 1\sigma_{\text{H}_2}^2$. Similarly if one H (say H_b) was far removed and the other H (H_a) moved close to the helium nucleus, then the energy dependence was in good agreement with previous calculations on $\text{He}(2^3\text{S})\text{-H}$. The important configurations were then $1s_{\text{He}} 2s_{\text{He}} 1s_{\text{H}_a} 1s_{\text{H}_b}$ and $1s_{\text{He}} 1s_{\text{H}_a}^2 1s_{\text{H}_b}$. For intermediate geometries we observed a smooth transition between these extremes.

Energies and widths have been calculated for several values of the coordinates R , θ , r illustrated in Figure 2. $\theta = 0^\circ$ corresponds to $C_{\infty v}$ and $\theta = 90^\circ$ corresponds to C_{2v} . We also calculated a few points for $\theta = 45^\circ$, which is an example of C_s symmetry. The complete results are listed in Table 7. SCF energies were also obtained for HeH_2^+ . Our basis set is not optimized for this calculation, of course, but nevertheless the energies obtained were in good agreement with the results of Brown and Hayes.²³ In addition, the present calculation includes a number of non-collinear geometries not investigated by Brown and Hayes.

Since our first scattering calculations will be based on the rigid rotator approximation to H_2 , we shall examine in more detail the "slice" of the potential surface corresponding to fixed $r = 1.4 a_0$ (the equilibrium H_2 bond length). In this case, one may expand the potential surface

$$V^*(R, \theta) = \sum_{\ell=0}^{\infty} v_{\ell}(R) P_{\ell}(\cos\theta) \quad (\text{even } \ell) \quad (30)$$

Since we calculated $V^*(R, \theta)$ for three values of θ at each R , we may assume that this series is truncated after $\ell = 0, 2, 4$ and thus solve for v_0, v_2 , and v_4 . The results of this procedure are plotted in Figure 3. Since $v_0 > v_2 \gg v_4$, the procedure seems justified. A similar procedure may be applied to the ionization width. Figure 4 shows the $\ell = 0$ and $\ell = 2$ terms of the width. Γ shows the typical exponential behavior calculated or estimated for other autoionizing molecules, although there is some leveling off at small R . The angular dependence of Γ is much less pronounced than the radial dependence.

Consideration of the r -dependence of the surface suggests that the dynamical treatment of the H_2 as a rigid rotator may not be too severe an approximation at thermal energies. We found that the equilibrium value of

r , for fixed R and θ , did not change significantly for $R \geq 6 a_0$. Even for the linear geometry at $R = 3 a_0$, the equilibrium value of r is only $0.12 a_0$ less than its value at $R = \infty$. This suggests that the electronic structure of H_2 is relatively unperturbed until $R \leq 3 a_0$. The dependence of Γ on r was smooth but not too pronounced. This is consistent with the approximation that the background continuum function was a coulomb wave centered at the midpoint of H_2 . The only dependence on r was indirect, through the energy of the continuum wave ($k^2/2$).

In most of our calculations, the desired resonance root of H_{QQ} was the lowest eigenvalue. The use of STO-s made this easy to verify by examining the components of the eigenvector. However, in certain cases, a higher root of H_{QQ} was identified as the proper one. This occurred when the H_2 bond length r was much greater than equilibrium. Then the bound resonance state is embedded in two continua: $He H H^+ + e^-$ and $He H^+ H + e^-$. This is because the σ_g and σ_u orbitals of H_2^+ are nearly degenerate for large r .

V. SUMMARY

We have presented a formalism well suited to practical computation in which autoionization occurs in a completely natural way as a transition between approximate eigenstates of $\hat{H}$ connected by the off diagonal elements $P\hat{H}Q$. Our choice of P and Q is such that the dominant contribution to the integrals for Γ comes from the inner region of physical space. In our formulation, therefore, the representation of H in a large basis of square integrable functions contains sufficient information to describe autoionization phenomena.

One of the advantages of the present method is that the exclusive use of square integrable basis functions to construct $\hat{H}$ afford a tremendous savings in computer time. The standard integrals must be evaluated only once for each internuclear separation. The only additional step is the evaluation of overlap integrals between the basis orbitals and the continuum orbitals. This may easily be done numerically.

The basic approximation in the present work is the simple form assumed for $P\chi_l$. Physical arguments have been made that this form is reasonable,^{8,9} and it is likely that in the sum over l some cancellation of error occurs. We plan to assess the accuracy of the present potential curves and widths by using them to compute Penning ionization cross sections which can be compared with experiment.

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Table L Basis sets of Slater-type orbitals for HeH calculations
(1)-(3) (first basis) and (4) (second basis)

(first basis)					(second basis)				
atom	n	l	m	zeta	n	l	m	zeta	
He	1	0	0	2.5	1	0	0	2.0	
He	1	0	0	1.5	1	0	0	1.0	
He	2	0	0	0.65	2	0	0	0.90	
He	2	0	0	0.45	2	0	0	0.61	
He	2	1	0	3.0	2	1	0,±1	2.0	
He	2	1	0	0.5	2	1	0,±1	0.61	
H	1	0	0	1.25	1	0	0	1.50	
H	1	0	0	0.85	1	0	0	1.00	
H	2	1	0	1.6666	2	1	0,±1	1.00	

Table II. Autoionizing Width Γ vs. Internuclear Separation R for HeH.

Calculation (2)^a

	R (a ₀)		
	2	4	8
I ₀	-2.682 x 10 ⁻²	4.156 x 10 ⁻³	1.953 x 10 ⁻⁵
I ₁	2.719 x 10 ⁻²	4.113 x 10 ⁻³	-2.756 x 10 ⁻⁵
I ₂	7.78 x 10 ⁻³	-5.846 x 10 ⁻³	1.772 x 10 ⁻⁴
I ₃	-3.813 x 10 ⁻³	-4.312 x 10 ⁻³	1.694 x 10 ⁻⁴
I ₄	-2.313 x 10 ⁻³	-1.216 x 10 ⁻³	-8.035 x 10 ⁻⁵
I ₅			-2.371 x 10 ⁻⁴
I ₆			-2.252 x 10 ⁻⁴
I ₇			-1.429 x 10 ⁻⁴
Γ	7.53 x 10 ⁻³	6.36 x 10 ⁻⁴	1.21 x 10 ⁻⁶

^a Calculation (2) is according to Eqs. 27-29 and includes the full continuum orbital.

Atomic units are used.

Table III. Autoionization Width Γ vs. Internuclear Separation R for HeH.Calculation (3).^a

	R (a ₀)					
	2	3	4	5	6	8
I ₀	-2.787 x 10 ⁻²	1.680 x 10 ⁻²	4.022 x 10 ⁻³	-3.523 x 10 ⁻⁴	1.170 x 10 ⁻⁴	3.552 x 10 ⁻⁵
I ₁	2.654 x 10 ⁻²	-5.243 x 10 ⁻³	3.601 x 10 ⁻³	-2.881 x 10 ⁻³	-1.177 x 10 ⁻³	8.000 x 10 ⁻⁶
I ₂	1.105 x 10 ⁻²	-1.536 x 10 ⁻²	-6.391 x 10 ⁻³	1.355 x 10 ⁻³	-1.834 x 10 ⁻⁴	8.937 x 10 ⁻⁵
I ₃	3.467 x 10 ⁻⁴	-6.034 x 10 ⁻³	-4.534 x 10 ⁻³	2.324 x 10 ⁻³	7.584 x 10 ⁻⁴	1.203 x 10 ⁻⁴
I ₄	-8.333 x 10 ⁻⁴	-1.281 x 10 ⁻³	-1.647 x 10 ⁻³	1.510 x 10 ⁻³	1.015 x 10 ⁻³	-9.328 x 10 ⁻⁵
I ₅	-3.234 x 10 ⁻⁴	-1.597 x 10 ⁻⁴	-3.993 x 10 ⁻⁴	6.313 x 10 ⁻⁴	6.902 x 10 ⁻⁴	-2.414 x 10 ⁻⁴
I ₆	-7.332 x 10 ⁻⁵	-6.830 x 10 ⁻⁶	-7.098 x 10 ⁻⁵	1.978 x 10 ⁻⁴	3.260 x 10 ⁻⁴	-2.279 x 10 ⁻⁴
I ₇		1.944 x 10 ⁻⁶	-9.500 x 10 ⁻⁶	5.000 x 10 ⁻⁵	1.196 x 10 ⁻⁴	-1.433 x 10 ⁻⁴
I ₈				1.064 x 10 ⁻⁵	3.613 x 10 ⁻⁵	-6.930 x 10 ⁻⁵
I ₉						-2.754 x 10 ⁻⁵
I ₁₀						-9.339 x 10 ⁻⁶
k	.81760	.58969	.56484	.59562	.62833	.66200
2πρ	4.8924	6.7832	7.0817	6.7157	6.3661	6.0423
Γ	7.85 x 10 ⁻³	3.96 x 10 ⁻³	6.62 x 10 ⁻⁴	1.24 x 10 ⁻⁴	2.32 x 10 ⁻⁵	1.02 x 10 ⁻⁶

^a Calculation (3) is according to Eqs. 27-29, but the non-square-integrable term involving $\phi_c^{(\ell)}$ is neglected. Results for $R = 2, 4$, and $8 a_0$ may be compared with Table II. k is the wave number of the ionized electron, and ρ is the density of states. Atomic units are used.

Table IV. Final Results for Autoionization Width Γ vs. Internuclear Separation
for HeII.^a

	R (a ₀)						
	2.0	2.5	3.0	3.5	4.0	6.0	8.0
I ₀	-2.988 x 10 ⁻²	2.695 x 10 ⁻²	1.822 x 10 ⁻²	-1.018 x 10 ⁻²	4.814 x 10 ⁻³	2.035 x 10 ⁻⁴	-3.732 x 10 ⁻⁵
I ₁	-3.282 x 10 ⁻²	2.130 x 10 ⁻²	9.098 x 10 ⁻³	-1.185 x 10 ⁻³	-2.379 x 10 ⁻³	1.264 x 10 ⁻³	-2.033 x 10 ⁻⁵
I ₂	1.052 x 10 ⁻²	-1.884 x 10 ⁻²	-1.762 x 10 ⁻²	1.299 x 10 ⁻²	-8.258 x 10 ⁻³	8.097 x 10 ⁻⁶	-7.792 x 10 ⁻⁵
I ₃	6.217 x 10 ⁻³	1.034 x 10 ⁻³	3.722 x 10 ⁻³	-4.356 x 10 ⁻³	4.087 x 10 ⁻³	-9.629 x 10 ⁻⁴	1.384 x 10 ⁻⁴
I ₄	-4.069 x 10 ⁻³	1.563 x 10 ⁻³	3.703 x 10 ⁻⁴	3.136 x 10 ⁻⁴	-7.998 x 10 ⁻⁴	1.041 x 10 ⁻³	7.632 x 10 ⁻⁵
I ₅	1.228 x 10 ⁻³	-6.670 x 10 ⁻⁴	-4.001 x 10 ⁻⁴	2.224 x 10 ⁻⁴	-3.188 x 10 ⁻⁵	-6.324 x 10 ⁻⁴	-2.482 x 10 ⁻⁴
I ₆	-2.540 x 10 ⁻⁴	1.604 x 10 ⁻⁴	1.227 x 10 ⁻⁴	-1.018 x 10 ⁻⁴	6.776 x 10 ⁻⁵	2.758 x 10 ⁻⁴	2.488 x 10 ⁻⁴
I ₇	4.067 x 10 ⁻⁵	-2.819 x 10 ⁻⁵	-2.503 x 10 ⁻⁵	2.572 x 10 ⁻⁵	-2.393 x 10 ⁻⁵	9.512 x 10 ⁻⁵	-1.628 x 10 ⁻⁴
I ₈	-5.348 x 10 ⁻⁶	+3.966 x 10 ⁻⁶	3.952 x 10 ⁻⁶	-4.803 x 10 ⁻⁶	5.590 x 10 ⁻⁶	2.732 x 10 ⁻⁵	8.125 x 10 ⁻⁵
I ₉						-6.750 x 10 ⁻⁶	-3.320 x 10 ⁻⁵
I ₁₀						1.467 x 10 ⁻⁶	1.155 x 10 ⁻⁵
k	.8153	.6646	.5906	.5680	.5721	.6404	.6728
2πρ	1.227	1.505	1.693	1.761	1.748	1.562	1.486
Γ	1.05 x 10 ⁻²	9.26 x 10 ⁻³	5.01 x 10 ⁻³	2.06 x 10 ⁻³	8.00 x 10 ⁻⁴	2.58 x 10 ⁻⁵	1.13 x 10 ⁻⁶

^a The notation is exactly the same as in Table III. The only difference is the use of a larger basis set.

Table V. Resonance energy for $\text{He}(2^3\text{S})-\text{H}$.^a

R	$V^*(R)$
2.0	-2.62442
2.5	-2.71241
3.0	-2.74419
3.5	-2.74987
4.0	-2.74395
6.0	-2.69897
8.0	-2.67744
25.0	-2.67394

^a These are the final results of calculation (4) in atomic units. The experimental dissociation limit is -2.67523 a.u.

Table VI. Basis set of Slater-type orbitals for the calculations on
 $\text{He}(2^3\text{S})-\text{H}_2$.^a

atom	orbital	zeta
He	1s	2.00
	1s	1.00
	2s	0.61
	$2p_x, 2p_y, 2p_z$	0.61
each H	1s	1.50
	1s	1.00
	$2p_x, 2p_y, 2p_z$	1.00

^a Each STO was expanded in 6 Gaussian-type orbitals.

Table VII. Results for V^* , V_+ , and Γ for HeH_2^a .

R	θ	r^b	V^*	Γ	V_+
3.0	0	1.00	-3.186143	6.06×10^{-3}	-3.309554
3.0	0	1.25	-3.216686	3.78×10^{-3}	-3.396816
3.0	0	1.30	-3.216311	3.47×10^{-3}	-3.407380
3.0	0	1.35	-3.214490	3.19×10^{-3}	-3.416385
3.0	0	1.40	-3.211431	2.95×10^{-3}	-3.424050
3.0	0	1.80	-3.158920	1.52×10^{-3}	-3.454388
3.0	45	1.40			-3.421032
3.0	90	1.00	-3.208059	7.34×10^{-3}	-3.304738
3.0	90	1.35	-3.255670	4.31×10^{-3}	-3.410330
3.0	90	1.40	-3.255828	4.03×10^{-3}	-3.417774
3.0	90	1.45	-3.255040	3.79×10^{-3}	-3.424046
3.0	90	1.80	-3.233047	2.60×10^{-3}	-3.445689
4.0	0	1.00	-3.240024	2.96×10^{-3}	-3.306871
4.0	0	1.30	-3.282371	1.98×10^{-3}	-3.405918
4.0	0	1.35	-3.282938	1.88×10^{-3}	-3.415042
4.0	0	1.40	-3.282363	1.80×10^{-3}	-3.422804
4.0	0	1.45	-3.280818	1.73×10^{-3}	-3.429387
4.0	0	1.80	-3.252838	1.48×10^{-3}	-3.453140
4.0	0	3.00	-3.175245		-3.436948
4.0	45	1.40	-3.289316	1.71×10^{-3}	-3.422144
4.0	90	1.00	-3.246569	2.88×10^{-3}	-3.305512
4.0	90	1.35	-3.294546	1.56×10^{-3}	-3.413793
4.0	90	1.40	-3.294770	1.40×10^{-3}	-3.421556

Table 7 continued.

4.0	90	1.45	-3.294043	1.35×10^{-3}	-3.428131
4.0	90	1.80	-3.272238	8.69×10^{-4}	-3.451666
5.0	0	1.40	-3.296840	4.23×10^{-4}	-3.421461
5.0	0	2.50	-3.222522	6.14×10^{-4}	-3.447638
5.0	0	3.00	-3.214261		-3.433381
5.0	0	4.00	-3.201510		-3.404606
5.0	45	1.40	-3.299139	3.67×10^{-4}	-3.421413
5.0	90	1.40	-3.300987	2.88×10^{-4}	-3.421385
6.0	0	1.00	-3.254250	9.15×10^{-5}	-3.305166
6.0	0	1.35	-3.301680	7.07×10^{-5}	-3.413280
6.0	0	1.40	-3.301857	6.96×10^{-5}	-3.420990
6.0	0	1.45	-3.301094	6.88×10^{-5}	-3.427517
6.0	0	1.80	-3.279458	6.91×10^{-5}	-3.450831
6.0	0	4.0	-3.200593		-3.403446
6.0	45	1.40	-3.302615	6.01×10^{-5}	-3.420994
6.0	90	1.00	-3.255096	8.10×10^{-5}	-3.304798
6.0	90	1.40	-3.303270	4.89×10^{-5}	-3.421038
6.0	90	1.80	-3.280749	3.66×10^{-5}	-3.451174
6.5	0	7.0	-3.202478		-3.370072
7.0	0	1.40	-3.304333	1.05×10^{-5}	-3.420802
7.0	45	1.40	-3.304538	8.97×10^{-6}	-3.420785
7.0	90	1.40	-3.304747	7.58×10^{-6}	-3.420827
7.5	0	7.0	-3.191493		-3.363930
8.0	0	1.00	-3.257331	1.57×10^{-6}	-3.304754
8.0	0	1.35	-3.305258	1.58×10^{-6}	-3.413002
8.0	0	1.40	-3.305482	1.62×10^{-6}	-3.420712

Table 7 continued.

8.0	0	1.45	-3.304760	1.66×10^{-6}	-3.427236
8.0	0	1.80	-3.283062	2.00×10^{-6}	-3.450479
8.0	45	1.40	-3.305513	1.32×10^{-6}	-3.420690
8.0	90	1.00	-3.257388	1.26×10^{-6}	-3.304600
8.0	90	1.40	-3.305565	1.10×10^{-6}	-3.420713
8.0	90	1.80	-3.282984	1.16×10^{-6}	-3.450615
9.0	0	1.40	-3.305947	2.46×10^{-7}	-3.420662
9.0	90	1.40	-3.305940	1.50×10^{-7}	-3.420653
10.0	0	1.40	-3.306108	3.82×10^{-8}	-3.420630
10.0	45	1.40	-3.306093	2.65×10^{-8}	-3.420622
10.0	90	1.40	-3.306087	1.89×10^{-8}	-3.420620
14.5	0	23.0	-3.206108		-3.368466
15.0	0	22.0	-3.200393		-3.360546
17.0	0	18.0	-3.134897		-3.358469
19.5	0	13.0	-3.129821		-3.358542
23.0	0	6.0	-3.129245		-3.369969
24.5	0	3.0	-3.160897		-3.431992
25.0	0	1.40	-3.306141		-3.420572
25.0	90	2.00			-3.453147
25.0	90	1.00	-3.257929		-3.304509
25.0	90	1.35	-3.305916		-3.412854
25.0	90	1.40	-3.306141		-3.420572
25.0	90	1.45	-3.305415		-3.427102
25.0	90	1.80	-3.283589		-3.450367

^a The energies for HeH_2^+ were determined from the SCF wave function. The exact asymptotic limits for these potentials are $V^*(R \rightarrow \infty, r = 1.4) = -3.3495$ a.u. and $V_+(R \rightarrow \infty, r = 2.0) = -3.5063$ a.u.

^b R, r, and θ are the coordinates defined in Figure 2.

Figure Captions

- Figure 1. Autoionization width Γ of $\text{He}(2^3\text{S})-\text{H}$, as a function of internuclear distance R . The solid line connects the points of the present work, and the dashed line connects the results of MSS (ref. 8).
- Figure 2. Coordinates (R, r, θ) specifying the configuration of $\text{He}(2^3\text{S})-\text{H}_2$.
- Figure 3. Legendre moments $U_\lambda(R)$, $\lambda = 0, 2, 4$, for the $\text{He}(2^3\text{S})-\text{H}_2$ potential energy surface (with r , the H_2 bond length, fixed at its equilibrium value $1.4 a_0$).
- Figure 4. Legendre moments Γ_λ , $\lambda = 0, 2$, of the autoionization width for $\text{He}(2^3\text{S})-\text{H}_2$ (with the H_2 bond length fixed at its equilibrium value).

XBL 769-4804

Figure 1

XBL 769-4803

Figure 2

XBL 769-4805

Figure 3

XBL 769-4806

Figure 4

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