

Multichannel Configuration Interaction Theory Applied to the $(n\ell 2) 1 S$ Autoionizing States of Helium

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TABLE I. Results of variational calculations on BN.

State	Configura- tion	Total energy (a.u.) at $R=2.7$ a.u.		r_e (Å)		E_{calc} (eV)		$E_{\text{calc}}+\Delta E_{\text{corr}}$ (eV)	
		This work	VRM	This work	VRM	This work	VRM	This work	VRM
$^3\Pi$	(II)	-78.97869	-78.97163	1.320 ^a	1.305	0	0	0	0
$^3\Sigma^+$	(III)	-78.89634	-78.89298	1.222	1.220	1.23	1.10	0.55	0.42
$^1\Pi$	(II)	-78.95993	-78.94436	1.328	1.306	0.59	0.60	0.59	0.60
$^3\Sigma^-$	(IV)	-78.98586	...	1.414	...	0.27	...	0.69	...
$^1\Sigma^+$	(I)	-78.86931	-78.86933	1.246	1.246	2.60	2.29	0.89	0.58

^a Experimental value is 1.281 Å. The high value of r_e obtained in this work is due to a relatively poor variational calculation at $R=2.25$ a.u. However, we are informed by Miss P. J. Briggs of King's College Chemistry

Department that, after taking account of interaction between all the singly excited $^3\Pi$ configurations (constructed from the MO's of this work), the value of r_e for the ground state was 1.301 Å.

depend only on the E_{calc} values. It will be seen that although the two variational calculations on the $^1\Sigma^+$ closed shell agree (as they should) to within 0.00002 a.u., the term energy of the $^1\Sigma^+$ state is 0.3 eV above the corresponding VRM value, which reflects the improved variational calculation of the $^3\Pi$ state in this work. Term values for the open-shell configurations, however, are not greatly affected by the better variational approach. The difference is about 0.1 eV for $^3\Sigma^+$ and is insignificant for $^1\Pi$.

The surprisingly low-lying $^3\Sigma^-$ state has been raised (relative to $^3\Pi$) to 0.69 eV by correlation energy differences, so that it need not be considered as a possible alternative ground state to $^3\Pi$, in agreement with recent experimental work.⁹

We are greatly indebted to Dr. Richards for giving us details of his calculations beyond those given in Ref. 1.

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Multichannel Configuration Interaction Theory Applied to the $(nl^2)^1S$ Autoionizing States of Helium

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The configuration interaction (CI) theory for autoionizing states given by Fano¹ has provided the basis for much of the experimental as well as other theoretical investigations. However, this theory has not been fully utilized as a computational method for investigating atomic and molecular systems, particularly in the energy region where more than one channel is accessible. The single direct application² known to the authors is limited to one open channel.

In the present work a generalized Fano CI technique is used to investigate the $(nl^2)^1S$ autoionizing states of helium. Energies, widths, probability amplitudes, and

wavefunctions of the form

$$\Psi_{jE} = \sum_k^N a_{jk}(E) \phi_k(\vec{r}_1 \vec{r}_2) + \sum_m^M \int b_{jm\epsilon}(E) \psi_{m\epsilon}(\vec{r}_1 \vec{r}_2) d\epsilon, \quad (1)$$

where ϕ_k and $\psi_{m\epsilon}$ are our initial approximations to the bound and continuum components, are obtained for states with $n=2-4$, $l \leq 2$ and $n=5$, $l=0$ with energies in the range 57.96–75.51 eV above the ground state (i.e., the region in which the $n=1-3$ channels are open). We use Hartree-Fock wavefunctions for the ϕ_k , and for $\psi_{m\epsilon}$ we use an appropriate combination of hydrogenic orbitals—unscreened (He^+) orbitals for the

TABLE I. Comparison of resonance energies and widths for the $(nl^2)^1S$ states with experiment and other theoretical results.

Method	$2s^2(22+)$		$2p^2(22-)$		$3s^2(33+)$		$3p^2(333d-)$		$3d^2(333d+)$	
	E_r^a	Γ^b	E_r	Γ	E_r	Γ	E_r	Γ	E_r	Γ
Close coupling without correlation ^c	57.86	0.1406	62.81	0.0188	69.37	0.0860	70.37	0.2246	72.04	0.0249
Close coupling with correlation ^d	57.84	0.124	62.13	0.0073	69.40	0.1650	70.44	0.4054		
Truncated diagonalization ^e	57.94		62.30		69.37		70.41		72.00	
This work ^f	57.96	0.1426 ± 0.0015	63.16	0.0029 ± 0.002	69.43	0.0730 ± 0.01	70.52	0.0048 ± 0.01	72.73	0.0326 ± 0.02
Experiments	57.82 ^g 57.9 ^{h,i}		62.15 ^g		69.8(?) ^j					
	$4s^2(44+)$		$4p^2(444d-)$		$4d^2(4f^2)$		$5s^2(55+)$			
	E_r	Γ	E_r	Γ	E_r	Γ	E_r	Γ		
This work ^f	73.58	0.0443 ± 0.02	73.96	0.0247 ± 0.02	74.64	0.0829 ± 0.04	75.51	0.0169 ± 0.015		

^a Resonance energy in electron volts above ground state.^b Width in electron volts.^c $n=2$ results: P. G. Burke and D. D. McVicar, Proc. Phys. Soc. (London) **86**, 989 (1965). $n=3$ results: Ref. 6.^d $n=2$ results: P. G. Burke and A. J. Taylor, Proc. Phys. Soc. (London) **88**, 549 (1966). $n=3$ results: Ref. 8.^e $n=2$ results: L. Lipsky and A. Russek, Phys. Rev. **142**, 59 (1966). $n=3$ results: Ref. 6.^f The uncertainty in Γ is that estimated from a convergence study with increasing numbers of nl^2 configurations and increasing k_{\max} [the upperlimit on the integral over the continuum orbitals, Eq. (1)]. Errors in Γ due to the absence of $nl'n'(n \neq n')$ and $n'kl(n' > n)$ configurations are difficult to evaluate and therefore not included in $\Delta\Gamma$. That uncertainty introduced by finite k_{\max} is the major component to $\Delta\Gamma$.^g M. E. Rudd, Phys. Rev. Letters **15**, 580 (1965).^h J. A. Simpson, G. E. Chamberlain, and S. R. Mielczarek, Phys. Rev. **139**, 1039A (1965).ⁱ N. Oda, R. Nishimura, and S. Takira, Phys. Rev. Letters **24**, 42 (1970).^j Reference 7.

bound electron and completely screened (H) orbitals for the unbound electron. The procedure for calculating the ϕ_k 's is given elsewhere.³ Integrals involving the unbound functions were evaluated by methods to be reported shortly.⁴

Unlike Fano's original theory, which assumes a knowledge of the intermediate bound and continuum states which diagonalize the total Hamiltonian in the subspace defined by the Feshbach⁵ projection operators, the theory used here is more general. Although the nonlocalized functions $\psi_{m\epsilon}$ are assumed to be orthonormal and to diagonalize some part of the total Hamiltonian, all other restrictions on φ_k and $\psi_{m\epsilon}$ have been removed.

In Table I we list our calculated positions and widths and compare them with those of other workers. The

configurations nl^2 are those from the independent particle model as determined from the relative position of each state within each cluster n . The level designations (i.e., $22\pm$) are those given by Ormonde, Whitaker, and Lipsky.⁶ For the $n=2$ and 3 states, agreement is quite good except for the widths of the states $22-$ and $333d-$. In the limit of strong coupling, the width of the $22-$ state is the difference between the geometric and arithmetic means of the widths of the $2p^2$ and $2s^2$ configurations and hence is relatively uncertain. We expect similar difficulties for all strongly coupled $(-)$ states.

Our resonance energies are consistently slightly higher than those obtained with other methods. Since our resonance energies do not represent rigorous upper

TABLE II. Probability for decay of the $(nl^2)^1S$ autoionizing states to the degenerate $(nkl)^1S$ open channel.

State	$1sks$	$2sks$	$2pkp$	$3sks$	$3pkp$	$3dkd$	Γ (eV)
$2s^2(22+)$	1.00						0.1426 \pm 0.0015
$2p^2(22-)$	1.00						0.0029 \pm 0.002
$3s^2(33+)$	0.333	0.465	0.202				0.0730 \pm 0.01
$3p^2(333d-)$	0.206	0.306	0.488				0.0048 \pm 0.01
$3d^2(333d+)$	0.016	0.206	0.779				0.0326 \pm 0.02
$4s^2(44+)$		0.142	0.182	0.246	0.383	0.048	0.0443 \pm 0.02
$4p^2(444d-)$		0.031	0.174	0.292	0.198	0.304	0.0247 \pm 0.02
$4d^2(4f^2)$		0.026	0.063	0.210	0.496	0.206	0.0829 \pm 0.04
$5s^2(55+)$		0.127	0.029	0.410	0.368	0.066	0.0169 \pm 0.015

bounds, we conclude that there is a positive electronic correlation error which can be accounted for by including the $nl'n'l'$ configurations. In spite of this our resonance energy for the $3s^2$ state falls below the lowest resonance feature of the experimental $1s-2s$ He electron impact cross section of Daly and Powell,⁷ which supports the remark of Burke and Taylor⁸ who suggest the energy scale of the Daly and Powell experiment is about 0.5 eV in error.

The authors are not aware of any $n=4$ results for comparison. The $4f^2$ state was found to be very near the $n=4$ threshold. Due to threshold effects⁹ which are not accounted for in the CI theory, we cannot reliably determine the $4f^2$ resonance parameters. The $5s^2$ state clearly lies below the $n=4$ threshold. This means ionization is accompanied by a change in principal quantum number by the electron left on the ion of at least two or more.

In Table II we give our results for the relative probability for decay to each channel as determined by the scattering amplitude matrix S . Since we are considering just the 1S wave, only the $nlkl$ 1S open channels are available for decay in $L-S$ coupling. The widths are repeated for convenience. It can be seen that the preferred decay mechanism involves the smallest change in principal quantum number of the helium ion (He^+) for all states studied here. But during decay it is evident an interelectronic transfer of orbital angular momentum may often occur. Physically this can be expected since during decay a large transfer of kinetic energy (linear momentum) between the incident and target electrons must also take place. The large mixing of the nl^2 and $nlkl$ configurations in the

interaction region where the transfer of momentum takes place accounts quantum mechanically for the large probability of transfer.

Our results and other more detailed supporting evidence to be reported subsequently suggest that the approximations made here are reasonable. They are: use of Hartree-Fock wavefunctions for the bound component and a product of hydrogenic functions for the nonlocalized component and the use of a limited number of bound configurations in the CI treatment.

Since our computer program can handle only five continua, the $1sks$ channel was omitted from the calculations for the states above the third threshold. The results suggest this has a negligible effect on the total width.

The calculations were performed on the CDC 6600 computer at the University of Minnesota Computer Center. One of us (DER) gratefully acknowledges their support and splendid cooperation.

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Absorption Spectrum of Ferrocene at 4.2°K*

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Although the absorption spectrum of ferrocene has been the subject of much study, agreement on the interpretation and number of bands present in the visible spectrum has not been good. Scott and Becker¹ have investigated ferrocene and nickelocene and have assigned the absorption bands at 4450 and 3250 Å to ligand field bands from the splitting of the d levels of Fe^{2+} . More recent experimental² and theoretical³ work support this assignment. Smith and Meyer achieved an increase in resolution by lowering the sample temperature in inert matrices.⁴ The absorption of crystals has been studied at room temperature⁵ and in liquid nitrogen.⁶ Low temperature crystal studies have been delayed by a destructive phase transition of the crystal in the neighborhood of 100°K. Recently Sohn *et al.*⁷ have measured the absorption spectrum of crystals at 4.2°K and have made an assignment of the electronic

spectrum. Their results show a resolution of the 3250 Å band into numerous vibrational bands similar to that previously reported⁴ but with considerable difference in vibrational spacing. They also noted the resolution of the 4400 Å band into a broad structureless band and a vibrationally structured one.

The purpose of this Note is to report the spectrum of ferrocene crystals at 4.2°K using crystals grown directly between quartz plates.⁸ This method of sample handling is slightly different from that of Sohn *et al.*, but the qualitative aspects of the spectra agree closely.

A one meter Czerny-Turner spectrograph was used with 103a F and 103a O plates to record the spectra. The spectrum in Figure 1 shows the 4.2°K absorption spectra. The room temperature and 77°K crystal spectra are shown for comparison. The vibrational bands in Regions I and III are of low contrast on the plates and