Wannier Analytic Continuation to Helium Negative Ion Resonances

A. M. Loughan and D. S. F. Crothers

Theoretical and Computational Physics Research Division, Department of Applied Mathematics and Theoretical Physics,
The School of Mathematics and Physics, The Queen's University of Belfast, Belfast, BT7 1NN, Northern Ireland

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The uniform, semiclassical wave function [D. S. F. Crothers, J. Phy. B **19**, 463 (1986)] has been analytically continued to below the energy threshold in order to calculate the complex eigenenergies for doubly excited states of helium using a complex Bohr-Sommerfeld quantization rule with at least one complex transition point. The real parts of the eigenvalues are in good agreement with the experimental results of Buckman *et al.* [S. J. Buckman *et al.*, J. Phys. B **16**, 4039 (1983); S. J. Buckman and D. S. Newman, J. Phys. B **20**, L711 (1987)] for the resonance positions while the imaginary parts give the explicit widths of the resonances from which intensities have been estimated. [S0031-9007(97)04807-2]

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The classical theory of Wannier [1] for the threshold behavior of electron impact ionization has become the primary focus for all discussions of processes involving two electrons near the threshold for double escape from the field of an ion. The central point of this theory, where the classical equations of motion are solved in terms of the hyperspherical variables defined by

$$\rho^2 = r_1^2 + r_2^2, \quad \alpha = \tan^{-1}\left(\frac{r_2}{r_1}\right), \quad \theta_{12} = \cos^{-1}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2), \tag{1}$$

is that the threshold escape of the two electrons is dominated by the configuration $\alpha \simeq \pi/4$, $\theta_{12} \simeq \pi$, which coincides with the saddle point of the potential of the combined electron-nucleus and electron-electron interactions. This saddle point lies on the ridge, given by $\alpha = \pi/4$ for all θ_{12} with $0 \leq \theta_{12} \leq \pi$, which has come to be known as the "Wannier ridge". It is now well established that for doubly excited states of helium the highly correlated two electron excitations manifest themselves as "Wannier ridge resonances" [2–5]. The possible existence of a series of negative ion resonances in which the two electrons reside at or near the Wannier ridge in a highly correlated state was first suggested by Fano [6]. Buckman *et al.* [4,5] have subsequently used this proposal to interpret long resonance series observed in electron scattering by helium at energies near to, and below, the single ionization energy threshold.

Semiclassical version of Wannier's theory were derived by Peterkop [7] and Rau [8] but Crothers [9] gave the first complete semiclassical uniform, quantal description of so-called Wannier threshold ionization and associated **absolute** differential and total cross sections. Details of Crothers' semiclassical approximation are given in [9] where, after adopting a transformation of the dependent variable, the Schrödinger equation is solved in direct analogy with Peterkop [7] by taking a JWKB (Jeffreys, Wentzel, Kramers, Brillouin) approximation for the final-state wave function. The ingoing final-state JWKB wave function takes the form

$$\Psi_f^{-*} = \frac{C^{1/2} \exp\{-\frac{1}{2}\, i \ln \Delta\theta_{12} - i[S_0 + \frac{1}{2}\, S_1(\Delta\alpha)^2 + \frac{1}{8}\, S_2(\Delta\theta_{12})^2]\}}{\bar{\omega}^{1/2} \rho^{5/2} \sin\alpha \cos\alpha}\,, \tag{2}$$

where, with $Z_0 = 3/\sqrt{2}$ and $\omega^2 = 2E + 2Z_0/\rho$,

$$\omega^2 \simeq \omega^2 - \omega \frac{d}{d\rho}(\ln u_2) + i\omega \frac{d}{d\rho}(\ln u_1)\,, \tag{3}$$

$$S_0 \simeq \int_0^\rho d\tilde{\rho}\, \bar{\omega}(\tilde{\rho})\,, \tag{4a}$$

and

$$S_i = \rho^2 \omega \frac{1}{u_1} \frac{du_i}{d\rho}\,, \qquad i = 1, 2\,, \tag{4b}$$

with $\sim$ indicating dummy variable of integration. u_1 and u_2 are the standard Peterkop [7] Wannier functions which are associated, respectively, with the radial and angular correlated motion of the two electrons. As in [9], the deviation of the hyperspherical angle α from its Wannier ridge value of $\pi/4$ is denoted by $\Delta\alpha = \alpha - \pi/4$ and the deviation of the mutual polar angle θ_{12} from its Wannier ridge value of π is denoted by $\Delta\theta_{12} = \pi - \theta_{12}$.

The purpose of the present work is to extend the semiclassical treatment of [9] for the unstable motion of a pair of electrons along the potential ridge to the near threshold capture excitation process

$$e^- + \mathrm{He} \rightarrow (\mathrm{He}^-)^*$$

in order to calculate the complex eigenenergies E_N of the high-lying doubly excited Rydberg states of He^- where the eigenvalue of the resonance takes the form

$$E_N = E_R^N - \frac{i}{2}\Gamma_N , \tag{5}$$

in which E_R^N is the resonance position and Γ_N is the lifetime. We view the doubly excited negative ion of helium as consisting of a positively charged core ($Z = 1$) comprising He$^+(1s)$, with two excited electrons in a highly correlated state of energy below the single ionization threshold of He but above the single ionization threshold of He$^-$, in line with the grandparent model of Schulz [10]. For the purpose of the present study the wave function in Eq. (2) has been analytically continued to negative energy to represent the two excited electrons, which have positions $\mathbf{r}_1$ and $\mathbf{r}_2$ while the core electron, with position $\mathbf{r}_3$, is represented by the ground state one-electron atom eigenfunction. The final-state wave function, including both ingoing and outgoing waves, with the Gans-Jeffreys [11,12] connexion formula applied at the classical turning point $\rho = 0$, is given by

$$\Psi_f^{-*} = \frac{C_N^{1/2} Y_{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) 2^{3/2} e^{-2r_3 - i/2 \ln \Delta\theta_{12}}/\sqrt{\pi}}{\rho^{5/2} \sin\alpha \, \cos\alpha} \times \frac{\sin[\int_0^\rho d\tilde{\rho}(\omega^2 - \omega\{\ln u_2 - i \ln u_1\}')^{1/2} + \frac{\rho^2}{2}\omega(\ln u_1)'(\Delta\alpha)^2 + \frac{\rho^2}{8}\omega(\ln u_2)'(\Delta\theta_{12})^2 + \frac{\pi}{4}]}{[\omega^2 - \omega\{\ln u_2 - i \ln u_1\}']^{1/4}} , \tag{6}$$

where $'$ indicates $d/d\tilde{\rho}$ or $d/d\rho$. The complex eigenenergy given in Eq. (5) is employed so that we now have

$$\omega^2 = 2E_N + \frac{2Z_0}{\rho} , \tag{7}$$

and the Wannier functions [7] take the form

$$u_1 = \rho^{m_{12}} {}_2F_1\left(m_{12}, m_{12} + 1;\ 2m_{12} + \frac{3}{2};\ -E_N\rho/Z_0\right), \tag{8a}$$

$$u_2 = \rho^{m_{22}} {}_2F_1\left(m_{22}, m_{22} + 1;\ 2m_{22} + \frac{3}{2};\ -E_{N\rho}/Z_0\right), \tag{8b}$$

where the function ${}_2F_1$ is a Gauss hypergeometric function [13], and m_{12} and m_{22} are the Wannier indices [7]. The wave function includes, for arbitrary l_1, m_1, l_2, m_2, the spherical harmonic factor $Y_{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$, Eq. (48) of [9]. The total angular moment L is zero for this calculation; however, the only restrictions on the magnitudes of the l values of the individual electrons are that they should be equal and less than the individual principal quantum numbers.

Exponential decay of the wave function is required beyond the two transition points of the resonating system, given by $\rho = 0$ and $\rho = -Z_0/E_N$, which is complex. This requires that on the ridge we have

$$\int_0^{-Z_0/E_N} d\rho \sqrt{\omega^2 - \omega\left(\frac{d}{d\rho}\ln u_2 - i\frac{d}{d\rho}\ln u_1\right)} = N\pi + \frac{\pi}{2} . \tag{9}$$

Therefore, the wave function has N nodes where N is a hyperspherical radial quantum number for the two excited electrons. On changing the dummy variable according to

$$\rho = \frac{-Z_0 x}{E_N} \tag{10}$$

and setting

$$c^4 = \frac{-2{Z_0}^2}{E_N} , \tag{11}$$

Eq. (9) becomes

$$c\int_0^1 dx\left(\frac{1}{x} - 1\right)^{1/4} \sqrt{c^2\left(\frac{1}{x} - 1\right)^{1/2} - \frac{d}{dx}\ln\frac{u_2}{u_1^i}} = N\pi + \frac{\pi}{2} , \tag{12}$$

which has been solved numerically by the complex Newton-Raphson method. The solution involves the removal of the obvious removable singularity at the lower end point and since the logarithmic derivative term, in the above integrand, is divergent for $x = 1$ it was necessary to use the analytic continuation of the Gauss hypergeometric function given by Eq. 15.3.b of [13]. Similar remarks apply to the derivative of Eq. (12) with respect to c.

The most extensive study of the resonance features of He^{-*} for $n = 3$ to $n = 8$, where n is the lower of the two principal quantum numbers n_1 and n_2, was made by Buckman *et al.* [4,5], in measurements of metastable-atom excitation. These experiments trace the occurrence of four strong resonances which occur in the $n = 3$ region through to $n = 8$ with an additional tentative observation of the lowest ^2S feature at $h = 9$. The lowest three (in energy) of these were classified [14–16] as intrashell resonances, with $n_1 = n_2$ while the final resonance was of the intershell type, with $n_1 \neq n_2$. For the purpose of comparison with experiment we use the terminology of Buckman *et al.* [4] where it has been found that the calculated eigenvalues correspond to those of experiment for

$$N = n_1 + n_2 - L - 1 . \tag{13}$$

Stability is maximized with equal sharing of energy $n_1 = n_2$, or almost equal sharing $n_2 = n_1 + 1$. Essentially, any partitioning of E into (E_1, E_2), where $E = E_1 + E_2$, is possible; equally well, any partitioning of $N + L + 1$ into (n_1, n_2) couples, where $N + L + 1 = n_1 + n_2$, is possible. To rephrase, in principle there can be strong mixing of such configurations. However, we are concerned with the partitioning relevant to the central resonance peak while recognizing that other (n_1, n_2) couples are involved in the broadening of the resonance.

The terminology used here corresponds to the correlated quantum numbers K, T, and A, which are now used as standard for the classification of such doubly excited states, according to [17]

$$_{\zeta}(K,T)_{\eta}^{A\,2S+1}L^{\pi} = {}_{n_2}(n_1 - 1, 0)_{n_1}^{0\ \ 1}S^{e}\,, \tag{14}$$

where ζ, denoted by n in Lin's notation, is the principal quantum number of the outer electron and η, denoted by N in Lin's notation, is the principal quantum number of the inner electron.

The results obtained from the present calculation are given in Table I and are compared with the results of Buckman *et al.* [4,5]. The energy values obtained for the lower of the ^2S resonance features correspond to values of N where $n_1 = n_2 = n$, while those of the higher ^2S resonance feature correspond to values of N where, for $n_1 = n$, $n_2 = n_1 + 1$.

In Table II, we compare our results (theory z) for the lower features with the table on p. 576 of Buckman and Clark [18]. Theory a [3] and theory b [19] are semiempirical, being based on generalized Rydberg-quantum-defect formulas. Theory c [20] is a multiconfiguration Hartree-Fock one. Theory d [21] is a diabetic molecular treatment and theory e [22] is an R-matrix calculation. For $n \in [6, 9]$, our results lie within experimental error. For $n \in [3, 5]$, our results are a little on the low side by 0.111, 0.057, and 0.007, respectively. For $n \in [3, 4]$ the R-matrix theory (e) [22] gives the best agreement. By the very nature of our near-threshold analysis, the accuracy of our results at the higher n values would be expected to exceed that for the lower n values.

In Table III we compare our relative intensities with those of Buckman and Newman [5]. For $N = 13$, 15, 17 we see that the ratio of the two sets of intensities has reached a stable converged value. Our intensity is taken as being proportional to $|E_N|\frac{1}{2}\Gamma_N$. This follows from the theory of Fano [23] (cf. also Cowan [24]) by which the autoionization transition probability rate is A^a, which is proportional to his $|\langle\phi|H|\psi_\epsilon\rangle|^2$ where ϕ is our Ψ_f^{-*} and ψ_ϵ is our ϕ_i. This in turn is proportional to $|E_N|$, upon normalizing ϕ. It follows that the intensity is proportional to the product of A^a and $\frac{1}{2}\Gamma_N$, the lifetime. By detailing balance, the intensity for electron capture to form the doubly excited state is given likewise. The energy behavior of $\langle\phi|\phi\rangle$ is obtained by integrating over the mutual polar angle and the hyperspherical angle by the method of steepest descent and by averaging over the rapidly varying $\sin^2$ term in the hyperspherical radial integral. It is noticeable that the $|E_N|^{m_{12}}$ term is canceled. By running our code up to $N \in [20, 30]$, we observe that $E_R^N \sim N^{-2}$. By running our code up to $N = 300$, we observe that eventually $\Gamma_N \sim N^{-3}$, whereas for $N \in [21, 29]$, $\Gamma_N \sim N^{-2.87}$. This N^{-2} and N^{-3} behavior is to be expected—for instance, by taking the small x behavior of u_1 and u_2 in Eq. (12), evaluating as a sum of two $_3F_2$ hypergeometric functions, and analytically continuing via Barnes complex contour integrals. The net effect is that $I_N \sim N^{-5}$ in comparison with results of Feagin and Macek [25], namely $N^{-5.254} = N^{-3-2m_{12}}$, Rau [26], namely $N^{-6.254}$, Heim and Rau [27], namely $N^{-6.5}$, and Buckman and Newman [5], namely for $N \in [13, 17]$ $N^{-5.2\pm0.7}$. However, this is a little bit academic since for $N \in [21, 29]$, our result is more like $N^{-4.89}$; nevertheless, for $N \in [13, 17]$ it is more like $N^{-4.88\pm0.01}$ well within the error bars of [5]. More significant therefore is the converged ratio of the experimental, and our Wannier results, of Table III, namely, $4.4(\pm0.1) \times 10^{-2}$ for $N \in [13, 17]$, which embraces an error tolerance of less than 3%.

In summary, we have analytically continued the above-threshold Wannier quantal ionization theory of [9] to below threshold Wannier quantal doubly excited states. We have presented results for

$$e^- + \mathrm{He}(1s^{2\,1}S) \rightarrow \mathrm{He}^-\big(1s(n_1 s n_2 s^2 S)\big)$$

doubly excited states, where for the principal series, $n_1 = n_2 = n$ and $N = 2n - 1$, $L = 0$, while for the subsidiary

TABLE I. Resonance position energies for $L = 0$, $n_1 = n$, $n_2 = n_1 \Rightarrow N = n_1 + n_2 - 1 = 2n - 1$, and for $L = 0'$, $n_1 = n$, $n_2 = n_1 + 1 \Rightarrow N = n_1 + n_2 - 1 = 2n$ since $N = n_1 + n_2 - |l_1 - l_2| - 1$, where $\mathrm{L} = |l_1 - l_2|$. The experimental values are from (a) Buckman *et al.* [4] and (b) Buckman and Newman [5] using their notation. The number in brackets indicates the error in the second and third decimal places.

		Present results resonance position energies (eV)			b	a
n	N	$L = 0$	N	$L = 0'$	$L = 0$	$L = 0'$
2	3	19.492			19.367(5)	
3	5	22.330	6	22.963	22.451(10)	22.881(05)
4	7	23.368	8	23.641	23.435(10)	23.667(05)
5	9	23.833	10	23.973	23.850(10)	23.983(10)
6	11	24.077	12	24.158	24.080(10)	24.176(10)
7	13	24.220	14	24.271	24.217(10)	24.288(10)
8	15	24.311			24.307(15)	
9	17	24.372			24.387(15)	

TABLE II. The experimental values (the number in brackets indicates the error in the second and third decimal places) are from Buckman *et al.* [4] and Buckman and Newman [5]; theory: *z* current results; (a) Rau [3]; (b) Lin and Watanabe [19]; (c) Komninos *et al.* [20]; (d) Rost and Briggs [21]; (e) Fon *et al.* [22].

			Theory					
n	*N*	Experiment	*z*	*a*	*b*	*c*	*d*	*e*
3	5	22.451(10)	22.330	...	...	22.432	22.774	22.439
4	7	23.435(10)	23.368	...	...	23.408	23.578	23.434
5	9	23.850(10)	23.833	23.857	23.865	23.843	23.879	...
6	11	24.080(10)	24.077	24.087	24.095	24.077	24.090	...
7	13	24.217(10)	24.220	24.223	24.230	24.213	24.219	...
8	15	24.307(15)	24.311	24.310	24.316	24.301	24.304	...
9	17	24.387(15)	24.372	24.369		24.361	24.362	...

series, $n_2 = n_1 + 1 = n + 1$ and $N = 2n$, $L = 0'$, in the notation of Buckman *et al.* [4].

In future publications we extend the theory to $L \neq 0$, in particular $L = 1$ and $L = 2$, also to other Wannier indices, for instances to those for

$$e^- + \mathrm{He}^+(1s\,^2S) \rightarrow \mathrm{He}(n_1 s n_2 s\,^2S)\,.$$

In a unique way, we have calculated complex eigenenergies whose imaginary parts give directly the lifetime of these Wannier doubly excited Rydberg states [8], and have obtained good agreement with experiment, previous theories having addressed the resonance energy positions only. Moreover, since conversely the theory of [9] for above-threshold ionization is the analytic continuation of our new below-threshold ionization theory, it reinforces our contention that our above-threshold ionization theory is a fully fledged quantal treatment of ionization. The fact that we use semiclassical asymptotic methods to derive the form Ψ_f^{-*} on the hyperspherical surface at infinity, at which the detectors of the two electrons must be placed, does not obviate our contention that we have formed a uniform semiclassical exact quantal description of the Wannier ridge states. This does not mean that the initial total wave function Ψ_i^+ cannot be improved using all the well known methods, whereas our ψ_ϵ or ϕ_i above is only a plane wave times a target wave function. Of course, it can. For instance, and of relevance especially to lower n_1 values, exchange could be included.

TABLE III. Relative intensity values for $L = 0$ resonances. The experimental values (the number of brackets indicates the error in the last and second last decimal places) are from Buckman and Newman [5].

	Relative intensity		
N	Experiment [5]	$\frac{1}{2}\Gamma_N\lvert E_R^N - \frac{i}{2}\Gamma_N\rvert$	Ratio
5	0.53(1)	0.0050	0.0094
7	0.048(1)	0.00099	0.021
9	0.0105(2)	0.00029	0.028
11	0.0021(3)	0.00011	0.052
13	0.0011(1)	0.000049	0.045
15	0.00054(12)	0.000024	0.044
17	0.00030(12)	0.000013	0.043

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