Quasi-projection-operator calculation of autoionization states of Li

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Calculations of positions of the first three ^2S, ^2P autoionization states of lithium are reported. The results agree with experimental values (available in four of the six cases) to almost four-place accuracy. A comment is included concerning the current status of quasiprojection optical-potential scattering calculations for nonresonant e-He phase shifts.

Recently Pegg *et al.*[1] have made measurements of some optically forbidden autoionization states of alkali metals. These measurements complement measurements of Ederer, Lucatorto, and Madden[2] of optically allowed autoionization states of Li, so that together the measured energies provide a testing ground for calculational theories of such states. To compare with the earlier experiment[2] we had done some calculations on Li, and motivated by the recent experiment,[1] we report here our results using the quasi-projection-operator technique.[3] At the same time we shall comment on the present status of application of quasiprojection optical potential to nonresonant scattering of electrons from helium.

The quasi-projection-operator technique[3] was introduced to avoid the twin problems of calculating autoionization states of $(N+1)$-electron–atom systems when $N \geq 2$. If viewed in their rigorous form as scattering resonances of electrons from N-electron targets, these difficulties have to do with (i) the identity of the scattered electron with the orbital electrons; (ii) the lack of an exact analytic solution for the (ground state) target wave function. Both of these reasons imply that one cannot construct a rigorous Q operator (whose eigenvalues coming from $QHQ\Phi_\lambda = \mathcal{E}_\lambda \Phi_\lambda$ define a discrete set of energies $\mathcal{E}_\lambda$ very close to the resonant energies E_λ) with all the properties demanded by the Feshbach theory,[4] specifically including the property of idempotency: $Q^2 = Q$.

The solution that we offered[3] was based on the realization that idempotency was not essential to the eigenvalue problem and that if one relaxed that condition, then a Rayleigh-Ritz variational problem defined by

$$\delta\left\{\frac{\langle \Phi \hat{Q}H\hat{Q}\Phi\rangle}{\langle \hat{Q}\Phi, \hat{Q}\Phi\rangle}\right\} = 0 \tag{1}$$

could continue to give rise to a discrete spectrum $\mathcal{E}_\lambda$, but would allow explicit construction of quasi-projection operators $\hat{Q}$ (in which then approximations of the target state can naturally be inserted). In the present calculation we use the explicit form (labelled $\hat{Q}_b$ in Ref. 3)

$$\hat{Q} = 1 - \sum_{i=1}^{N+1} P_i \ , \tag{2}$$

where

$$P_i = \phi_0(x_i^{-1})\rangle\langle\phi_0(x_1^{-1}) \ . \tag{3}$$

ϕ_0 represents the ground state of the N-particle target system with the x_i^{-1} signifying the absence of spin and space coordinates x_i of the ith particle from among the $N+1$ particles of the compound system. [Further details are given in Ref. 3. It is emphasized the eigenvalues of the $\hat{Q}H\hat{Q}$ only correspond to resonances if they lie *below* the first inelastic threshold of the target, which in the present case is $Li^+(2^3S)$ at 64.4148 eV.]

Calculations here are based on closed-shell approximation of the ^1S ground of the (Li^+) target system:

$$\varphi_0 = (\zeta^3/\pi)e^{-\zeta(r_1+r_2)}, \tag{4}$$

where φ_0 is the spatial part of ϕ_0; the nonlinear parameter which minimizes the target energy is given by $\zeta = Z - \frac{5}{16}$, Z being the charge on the target nucleus ($Z = 3$ here).

The total wave function for the compound Li system is of the configuration interaction form

$$\Phi_{L,\,S=1/2} = \frac{\mathcal{A}}{\sqrt{3}}\left\{\sum_{\{n\}=1}^{N_\lambda} C_{\{n\}} R_{n_1 l_1}(r_1)R_{n_2 l_2}(r_2)R_{n_3 l_3}(r_3) \times \mathcal{Y}(l_1 l_2; l_3; L)\mathcal{S}(\tfrac{1}{2}\tfrac{1}{2}S_1, \tfrac{1}{2}; \tfrac{1}{2})\right\} \tag{5}$$

with Slater-type radial orbitals: $R_{nl}(r) = e^{-\alpha_{nl} r} r^{n-1}$. Changing Z to 3 from our original e-He calculation[3] both in the Hamiltonian H as well as in Eq. (4) for ζ, we minimized $\hat{Q}H\hat{Q}$, Eq. (1), as a function of numbers of configurations N_λ and of the nonlinear parameters. Table I gives examples of some results for the lowest three ^2S states. (Similar convergence is also obtained for ^2P states.) Each eigenvalue was minimized separately with

TABLE I. ^2S energies and widths of Li vs number of terms N_λ in Eq. (5).

N_λ	$\mathcal{E}_1$ (Ry)	Γ_1 (eV)	$\mathcal{E}_2$ (Ry)	Γ_2 (eV)	$\mathcal{E}_3$ (Ry)	Γ_3 (eV)
8	−10.7963	0.0552	−10.3676	0.0245	−10.2844	4×10^{-4}
16	−10.7984	0.0496	−10.3776	0.0165	−10.2886	3×10^{-5}
28	−10.8093	0.0381	−10.3848	0.0120	−10.2981	0.023
40	−10.8126	0.0423	−10.3970	0.0091	−10.3027	···

respect to a partial search of the nonlinear parameters. For each resulting wave function the width was calculated from

$$\Gamma_\lambda = 2k|\langle \hat{P}\Psi'|H|\hat{Q}\Phi_\lambda\rangle|^2 \tag{6}$$

where $\hat{P}\Psi' = \Psi'$ is a nonresonant scattering function derived from the exchange approximation using the same closed-shell ϕ_0.

One sees that as opposed to the positions, which are converging well, the widths are more sensitive, and only for the lower λ states can one reasonably claim to have a sufficiently stable result. We believe this is related to the general question of nonresonant scattering using the quasi-optical potential (see below). As a result in Table II, where we have collected our best results, we omit widths for those states where there is an absence of stability.

Referring to Table II, we see that the calculation is in agreement with experiment to about three and a half significant figures. On the whole these are the most satisfactory results of those so far calculated; however because of the limitations primarily of the target wave function, it is not warranted to press such comparisons too far.

Insofar as we have confidence in our width results, it is interesting that there is agreement with the one other calculated width for the $^1P(1)$ state.[5] It would clearly be desirable to have experimental widths, but from the theoretical point of view the width integral has a more fundamental significance. As noted in our original paper,[3] given a complete set (for a given N_λ and set of nonlinear parameters) of eigenfunctions Φ_λ and $\mathcal{E}_\lambda$, one can straightforwardly construct a quasi-optical potential from the optical potential[4]

$$v_{op} = PHQ\frac{1}{E-QHQ}QHP \tag{7}$$

by replacing P and Q by $\hat{P}(=1-\hat{Q})$ and $\hat{Q}$ and inserting the "complete set"

$$\sum_{\lambda=1}^{N_\lambda} Q\Phi_\lambda\rangle\langle\Phi_\lambda Q$$

on either side of $(E-\hat{Q}H\hat{Q})^{-1}$. In this way one generates the quasi-optical potential

$$\hat{v}_{op} = \sum_{\lambda=1}^{N_\lambda}\frac{\hat{P}H\hat{Q}\Phi_\lambda\rangle\langle\Phi_\lambda\hat{Q}H\hat{P}}{E-\hat{\mathcal{E}}_\lambda}. \tag{8}$$

Using this potential one has a well-defined scat-

TABLE II. Position of autoionization states of Li (in eV) compared to experiment and other calculations (relative to the Li ground state at −14.956 050 Ry [f]).

State	This calc.	Other calcs.		Experiment	
$^2S(1)$	56.3677	56.43 [a]		56.31 [b]	
	$\Gamma = 0.04$				
$^2S(2)$	62.0220				
	$\Gamma = 0.009$				
$^2S(3)$	63.3052				
$^2P(1)$	58.9383	58.96 [c]	58.96 [d]	58.91 [b]	58.91 [e]
	$\Gamma = 0.007$		$\Gamma = 0.007$		
$^2P(2)$	60.4960	60.60 [c]		60.40 [b]	60.396 [e]
$^2P(3)$	62.4879	62.46 [c]		62.42 [b]	62.419 [e]

[a] B. R. Junker, quoted in Ref. 1.
[b] Pegg *et al.*, Ref. 1.
[c] A. Weiss, quoted in Refs. 1 and 2.
[d] Barden, Bottcher, and Schneider, Ref. 5.
[e] Ederer, Lucatorto, and Madden, Ref. 3.
[f] S. Larsson, Phys. Rev. 169, 49 (1968).

tering equation for the scattering wave function

$$\Psi_L = \mathcal{A}\{U_L(i)\,\phi_0(i^{-1}) + \Phi(1,\ldots,N+1)\}$$

with asymptotic form

$$\lim_{r_i\to\infty} \Psi_L = \lim_{r_i\to\infty} \hat{P}\Psi_L = U_L(i)\phi_0(i^{-1}).$$

In particular the phase shift may be determined from

$$U_L(i) = [u_L(r_i)/r_i]Y_{L0}(\Omega_i)\chi_{1/2}(i)$$

in the usual way:

$$\lim_{r\to\infty} u_L(r) = \sin(kr - \tfrac{1}{2}\pi L + \eta_L)\,, \tag{9}$$

where u_L satisfies

$$\left(-\frac{d^2}{dr^2} + \frac{L(L+1)}{r^2} + V_H(r) - k^2\right)u_L + r\langle\phi_0|\,V_e + \hat{\mathcal{U}}_{\rm op}\,|P\Psi\rangle = 0\,. \tag{10}$$

V_H and V_e are the static and exchange potentials coming from the asymptotic part, $\mathcal{A}\{U_L\phi_0\}$, of Ψ_L, and $\mathcal{U}_{\rm op}$ is given in Eq. (8).

We have solved (10) for S-wave e-He scattering based on the eigenvector sets deriving from our earlier calculations.[3] As expected we find that the phase shifts increase as we increase N_λ *but* the phase shifts seem too large. For $N_\lambda = 12$ we are already 3% larger than the S phase shifts on Sinfailam and Nesbet,[6] which is generally conceded to be the best multiconfiguration calculation of e-He scattering (using, however, a closed-shell-type target state wave function). Unlike the present method that method relies on the region of stability of results as basis size is increased and parameters are varied. We have also used the angle-independent correlation function,[3] whose spatial part is given by

$$\Phi(r_1 r_2; r_3) = e^{-\alpha(r_1+r_2)-\gamma r_3}\sum_l^{N\lambda} C_{lmn}(r_1^l r_2^m + r_1^m r_2^l)r_3^n\,.$$

Such a function allows a much more thorough search of the nonlinear parameter space. There too we were led to phase shifts which are larger than those of Sinfailam and Nesbet,[6] but by a smaller amount than the configuration interaction ones. We cannot yet say whether we have convergence as N_λ is increased (and that to our mind is the central question), but we are finding that the percentage increases over Ref. 6 get larger as k is *decreased*. We suspect that this is related to the fact that our widths get more erratic the more removed the resonant state is from the lowest one. For the width integral is essentially the same as those occurring in the numerator of $\mathcal{U}_{\rm op}$, Eq. (8). And the further the energy E is removed from a specific resonance ($\mathcal{E}_\lambda$), the more important will be the higher terms in (8) relative to the lowest one. This explanation assumes that the major factor affecting the "width" integrals in the numerator of the optical potential is the resonance functions Φ_n rather than the scattering functions ψ_E. Indeed one may cogently argue that this is so as follows: In the scattering region the nonresonant continuum functions necessarily change only slowly with E, since the range of E is small where resonances occur below the first excited threshold. Nevertheless the fact that the lower widths are stable whereas the higher ones are not indicates that it is the Φ_n for higher n that are responsible. Since Φ_n are independent of E, the same inadequacy will also apply to them at small E as well. For in that region the total wave ψ_E is nonresonant in character and therefore one may reasonably attribute to it the same insensitivity as the nonresonant continuum.

The program used in computing $\hat{\mathcal{E}}_\lambda$ from (5) is that of Browne and Matsen[7] as modified for $\hat{Q}H\hat{Q}$ by J. N. Bardsley. We would like to thank Dr. Bardsley for having made this program available to us.

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