Doubly excited states of H⁻ and He in the coupled-channel hyperspherical adiabatic approach

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Doubly excited states (DES) of heliumlike systems are studied within the coupled-channel hyperspherical adiabatic approach. The results of the multichannel calculations of the $^1S^e$ and $^1P^o$ DES of H⁻ and He converging to the second ($n=2$) threshold are presented and compared with those found in literature.

In this paper we study the doubly excited states (DES) of heliumlike systems using the hyperspherical adiabatic (HSA) approach proposed in 1968 by Macek [1] for describing the spectrum of helium atom. This approach has been applied widely for studying the effects of electron correlations in the processes of excitation and ionization of two-electron systems (see reviews [2,3]). In most of the calculations with the HSA approach the adiabatic approximation is used neglecting the nonadiabatic coupling of channels in the system of radial equations (see, for instance, Refs. [1–6]). To get accuracy comparable with other known approaches one should take nonadiabatic effects into account [7–12]. The rapid convergence of the HSA expansion established in Refs. [10–12] enables one to get high accuracy ($\leq 10^{-4}$ a.u.) of the spectral characteristics of two-electron atoms using only a few radial equations. In this paper we apply the coupled-channel HSA approach to study the low-lying DES of H⁻ and He for which nonadiabatic effects are essential.

In the HSA approach the total two-electron wavefunction Ψ expansion in the hyperspherical coordinates $\{R,\Omega\}$ has the form [1,2]

$$\Psi(R,\Omega)=R^{-5/2}\sum_{\mu=1}^{N_R} F_\mu(R)\Phi_\mu(\Omega;R) ,$$

$$R=(r_1^2+r_2^2)^{1/2} , \quad \Omega\equiv(\alpha,\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) , \tag{1}$$

$$\alpha=\arctan(r_2/r_1) , \quad \hat{\mathbf{r}}_i=\{\theta_i,\phi_i\} , \quad i=1,2 .$$

Basis functions $\Phi_\mu \in L^2$ ($S^5(\Omega)$), where L^2 represents here the space of quadratically integrated functions and S^5 represents a five-dimensional sphere in six-dimensional space $\mathbb{R}^6$, can be expanded [1] over the standard bipolar harmonics $\mathcal{Y}_i^{LM}\equiv \mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2)$, $\{l_1,l_2\}\in[0,l_{max}]$, for the states $^{2S+1}L^\pi$ with a fixed total angular momentum L, parity π, and spin S,

$$\Phi_\mu(\Omega;R)=(\sin\alpha\cos\alpha)^{-1}\sum_{i=1}^{N_\alpha} g_i^{(\mu)}(\alpha;R)\mathcal{Y}_i^{LM}(\hat{\mathbf{r}}_1,\hat{\mathbf{r}}_2) . \tag{2}$$

To calculate the radial functions $\{F_\mu(R)\}_{\mu=1}^{N_R}$ and the angular ones $\{g_i^{(\mu)}(\alpha;R)\}_{i=1}^{N_\alpha}$, one should solve two corresponding spectral problems [(A) and (B)] for systems of coupled ordinary differential equations with fixed boundary conditions imposed on the finite intervals $R\in[0,R_{max}]$ and $\alpha\in[0,\pi/4]$ [1,8,11,12], respectively.

In the present work the numerical solution of spectral problems (A) and (B) has been carried out by the method of finite elements and by the method of finite differences, respectively. Construction of the net, approximation, solution of an algebraic eigenvalue problem, and the program realization are considered in detail in Ref. [13]. While solving the Sturm-Liouville problem (B) for angular functions $\{g_i^{(\mu)}(\alpha;R)\}_{i=1}^{N_\alpha}$ we have used the following values of the numerical scheme parameters [number of differential equations N_α (or number of bipolar harmonics l_{max}) and number of mesh points n_α of the finite-difference net]: (a) for H⁻ $^1S^e$, $N_\alpha=8$ ($l_{max}=7$) and $n_\alpha=440$, (b) for H⁻ $^1P^o$, $N_\alpha=6$ ($l_{max}=3$) and $n_\alpha=700$; (c) for He $^1S^e$, $N_\alpha=9$ ($l_{max}=8$) and $n_\alpha=500$ (d) for He $^1P^o$, $N_\alpha=8$ ($l_{max}=4$) and $n_\alpha=720$. To calculate derivatives of the HSA functions with respect to R we used finite-difference formulas of the fourth order of accuracy and the resulting tabulated potentials were interpolated by the cubic spline. For a finite-element approximation of radial spectral problem (A) the isoparametric Lagrange elements of the fourth order have been used [12,13].

In the present paper, to classify the DES we have used the HSA classification [12] based on the general classification of the HSA basis states [14]. In accordance with this classification the DES are denoted by the $^{2S+1}L^\pi$ $v(n,q)_p$ symbol. Here v implies the quantum number of the energy-level sequence in a given potential curve, the quantum number n is associated with the channel threshold, q is the quantum number corresponding to the eigenvalues of the dipole motion integral [12,15,14], and the value of $p=\pi(-1)^S$ connects gerade ($p=+1$) and ungerade ($p=-1$) HSA states with the value of the

TABLE I. Correspondence between different classifications of two-electron DES near the second threshold. Values L, S, and π are common for all schemes. Other quantum numbers used for the DES classification have the following meaning: n is the principal quantum number of the separated atom, $\bar{n}$ is the principal quantum number of an outside electron, and the index $\alpha=a,b,c$ denotes different resonant series, $K=n_2-n_1$, $T=m$, where n_1,n_2,m are parabolic quantum numbers, $A=\pm1,0$. Other quantum numbers are explained in the text.

State $2S+1L^\pi$	Lowest number of series $\bar{n}$	Cooper, Fano, and Prats[a]	Lipsky and Conneely[b] $(n,\bar{n},\alpha)$	Lin[c] $\bar{n}(K,T)_n^A$	This work $v(n,q)_p$
$^1S^e$	2	$2s\bar{n}s+2p\bar{n}p$	$(2,\bar{n},a)$	$\bar{n}(1,0)_2^+$	$v(2,0)_g$
	2	$2s\bar{n}s-2p\bar{n}p$	$(2,\bar{n},b)$	$\bar{n}(-1,0)_2^+$	$v(2,1)_g$
$^1P^o$	2	$2s\bar{n}p+\bar{n}s2p$	$(2,\bar{n},a)$	$\bar{n}(0,1)_2^+$	$v(2,1)_u$
	3	$2s\bar{n}p-\bar{n}s2p$	$(2,\bar{n},b)$	$\bar{n}(1,0)_2^-$	$v(2,0)_u$
	3	$2p\bar{n}d$	$(2,\bar{n},c)$	$\bar{n}(-1,0)_2^0$	$v(2,2)_u$

[a]Reference [18].
[b]References [16,24].
[c]Reference [17].

TABLE III. Dependence of the energy values (in a.u.) of the H^- $^1P^o$ DES near the $n=2$ threshold on the number of radial equations N_R.

N_R	State		
	$0(2,0)_u$	$1(2,0)_u$	$0(2,1)_u$
1	$-0.124\,901\,4$	$-0.124\,708\,7$	$-0.124\,265\,2$
2	$-0.124\,901\,4$	$-0.124\,708\,7$	$-0.124\,348\,0$
3	$-0.125\,921\,3$	$-0.125\,021\,6$	$-0.124\,350\,2$
4	$-0.125\,932\,5$	$-0.125\,022\,2$	$-0.124\,350\,7$
Other calculations	$-0.125\,955$[a]	$-0.125\,03$[a]	$-0.123\,82$[a]
	$-0.125\,96$[b]		
	$-0.125\,965$[c]	$-0.125\,015$[c]	$-0.124\,34$[c]
	$-0.125\,972\,6$[d]	$-0.125\,023\,3$[d]	
	$-0.126\,048$[e]		$-0.124\,351$[e]
	$-0.126\,098$[f]	$-0.125\,201$[f]	

[a]Reference [4].
[b]Reference [9].
[c]Reference [26].
[d]Reference [27].
[e]Reference [28].
[f]Reference [29].

spin S indicating an additional g or u parity of the basis HSA functions under the interchange of electrons. The correspondence between the HSA and other classifications of two-electron DES near the second threshold is given in Table I. The comparison between different classification schemes [3,16–18] of the DES and the peculiarities of the HSA classification in adiabatic and diabatic representations have been described in Ref. [12].

The results of calculations of the energies $^1S^e$ and $^1P^o$ DES of H^- versus the number of radial equations N_R are compared with other theoretical calculations in Tables II and III. It is seen from Table II that for the $^1S^e$ states

TABLE II. Dependence of the energy values (in a.u.) of the H^1S^e DES below the second ($n=2$) threshold on the number of radial equations N_R.

N_R	State		
	$0(2,0)_g$	$1(2,0)_g$	$2(2,0)_g$
1	$-0.148\,630$	$-0.125\,865$	$-0.124\,855$
2	$-0.147\,168$	$-0.125\,768$	$-0.124\,847$
3	$-0.148\,098$	$-0.125\,828$	$-0.124\,863$
4	$-0.148\,598$	$-0.125\,969$	$-0.124\,900$
5	$-0.148\,654$	$-0.125\,993$	$-0.124\,907$
6	$-0.148\,665$	$-0.125\,995$	$-0.124\,909$
Other calculations	$-0.148\,782$[a]		
	$-0.147\,896$[b]	$-0.125\,973$[b]	$-0.125\,012$[b]
	$-0.148\,777$[c]		
	$-0.148\,695$[d]	$-0.126\,015$[d]	$-0.124\,662$[d]
	$-0.148\,79$[e]	$-0.125\,845$[e]	

[a]Reference [20].
[b]Reference [16].
[c]Reference [21].
[d]Reference [25].
[e]Reference [6].

the adiabatic approximation gives very good energy values. Switching on the coupling with the second channel somewhat shifts the energy levels upwards, the value of this shift rapidly diminishing with increasing number of the level v. This means that angular correlations become weaker with increasing v. Inclusion of the third shell and further increase of the number of equations changes the energy value only in the fifth or sixth digit after the point, i.e., inclusion of three shells (six states of the HSA basis) provides accuracy of calculations not worse than 10^{-4} a.u. The results thus obtained agree well with the results of other calculations with the inclusion of a larger number of states.

Consider now $^1P^o$ resonances in the e^--H scattering. The analysis of Table III shows that the behavior of these
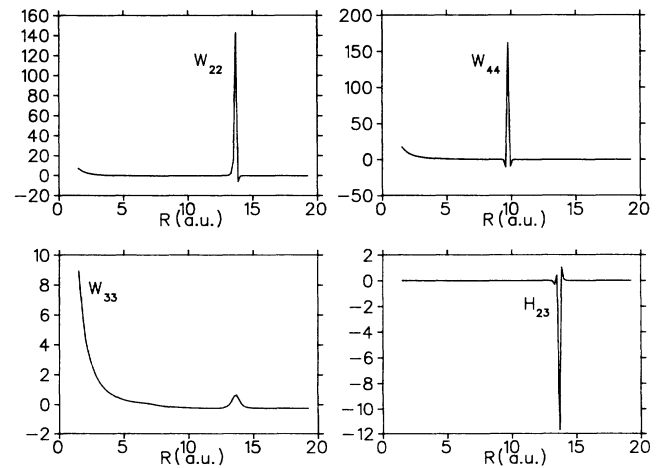

FIG. 1. Effective potentials $W_{\mu\mu}(R)=H_{\mu\mu}(R)+U_\mu(R)$ $-0.25R^{-2}$ (in Ry) for $\mu=2,3,4$ and matrix element $H_{\mu\nu}(R)=\langle\partial\Phi_\mu(\Omega;R)/\partial R\,|\partial\Phi_\nu(\Omega;R)/\partial R\rangle$ of the radial coupling between the second ($\mu=2$) and the third ($\nu=3$) channels for H^- $^1P^o$

TABLE IV. Energy levels $-E$ (in a.u.) of the He $^1S^e$ DES below the $n=2$ threshold.

State $v(2,q)_g$	Present work			Conneely and Lipsky[a]	Burke and McVicar[b]	Bhatia and Temkin[c]	Ho[d]	Oza[e]	Macias and Riera[f]
	One channel	Three channels	Six channels						
$0(2,0)_g$	0.772 151	0.778 002	0.778 824	0.775 245	0.7762	0.778 813	0.777 87	0.7778	0.778 405
$1(2,0)_g$	0.584 316	0.589 393	0.590 158	0.588 142	0.5871	0.590 079	0.589 92	0.589 86	0.589 925
$2(2,0)_g$	0.542 052	0.544 563	0.544 863	0.544 019	0.5427			0.544 87	0.544 878
$0(2,1)_g$	0.605 546	0.619 825	0.621 927	0.615 133	0.5945	0.622 748	0.621 98	0.620 52	0.619 277
$1(2,1)_g$	0.543 870	0.547 582	0.547 849	0.546 940	0.5440	0.548 234	0.548 09	0.547 87	0.547 759
$2(2,1)_g$	0.525 622	0.526 640	0.527 507	0.527 203	0.5257			0.527 62	0.527 586

[a]Reference [16].
[b]Reference [30].
[c]Reference [20].
[d]Reference [21].
[e]Reference [23].
[f]Reference [25].

resonances, identified with different potential curves near the second threshold, differs greatly. For the $^1P^o$ $0(2,1)_u$ shape resonance, switching on the coupling with the second channel lowers the adiabatic value of the energy by 10^{-4} a.u. Further increase in the number of channels changes only the fifth or sixth digit after the point. For the Feshbach resonances $^1P^o$ $v(2,0)_u$ ($v=0,1$) below the $n=2$ threshold, the adiabatic approximation provides energy values above the channel threshold; only inclusion of a strong coupling between the second and third channels shifts these resonances down below the threshold. A strong coupling between the second and the third channels is due to the presence of the quasicrossing point at $R=13.66$ between the potential curves $(2,0)_u$ and $(2,1)_u$, which results in pronounced maxima of the matrix elements of the radial coupling in the vicinity of this point (see Figs. 1 and 2). A standard way of removing singularities of the matrix elements at quasicrossings is passing to

the diabatic representation [2,9] in which quasicrossings become exact crossings. This allows one to calculate the spectra of DES with the required accuracy in the one-channel approximation [2–5,9,19], especially for high-lying states [6]. In the present paper we have calculated the positions of the $^1P^o$ shape and Feshbach resonances using the procedure of diabatic interpolation [1,4] of potentials in the region $11 < R < 15$. We have gotten the following energy values: -0.124372 a.u. for the shape resonance and -0.126019 and -0.125020 a.u. for the first two Feshbach resonances, respectively. These values are in good agreement with analogous calculations of Lin [4] and Christensen-Dalsgaard [9] (see also Ref. [19]), with the four-channel HSA calculation of the present paper and with the results of other calculations (see Table III).

Tables IV and V represent the results of the energy-level calculations of $^1S^e$ and $^1P^o$ DES of He, including a

TABLE V. Energy levels $-E$ (in a.u.) of the He $^1P^o$ DES below the $n=2$ threshold.

State $v(2,q)_u$	Present work		Lipsky and Conneely[a]	Burke and McVicar[b]	Bhatia and Temkin[c]	Ho[d]	Oza[e]	Macias and Riera[f]
	One channel	Four channels						
$0(2,0)_u$	0.668 367	0.692 842	0.688 36	0.6883	0.692 89	0.693 13	0.6928	0.692 13
$1(2,0)_u$	0.556 999	0.563 976	0.562 92	0.5625	0.563 89	0.5640	0.564 01	0.563 79
$2(2,0)_u$	0.530 722	0.534 367	0.533 86	0.5335			0.534 32	0.534 25
$0(2,1)_u$	0.550 229	0.597 014	0.586 56	0.5963	0.597 08	0.597 07	0.597 07	0.597 30
$1(2,1)_u$	0.527 573	0.546 450	0.546 21	0.5448			0.546 47	0.546 13
$2(2,1)_u$	0.517 815	0.527 351	0.527 13	0.5263			0.527 29	0.527 11
$0(2,2)_u$	0.545 163	0.547 096	0.546 81	0.5462		0.546 92		0.547 01
$1(2,2)_u$	0.526 375	0.527 513	0.527 45	0.5270				0.527 55
$2(2,2)_u$	0.517 343	0.518 014	0.518 02					0.517 87

[a]Reference [24].
[b]Reference [30].
[c]Reference [22].
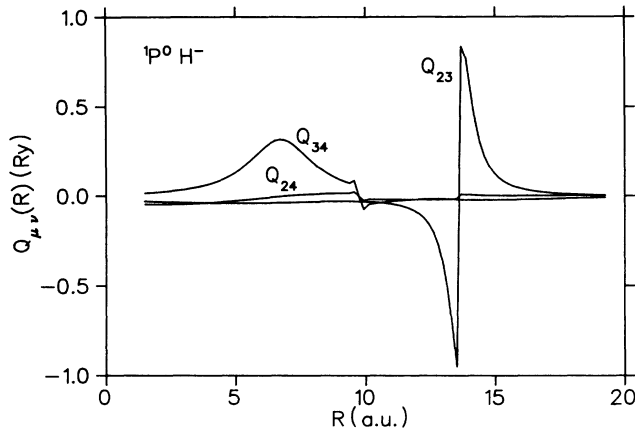[d]Reference [21].
[e]Reference [23].
[f]Reference [29].

FIG. 2. H^- $^1P^o$ matrix elements $Q_{\mu\nu}(R)$ $= \langle \Phi_\mu(\Omega;R) | \partial \Phi_\nu(\Omega;R) / \partial R \rangle$ for $\mu=2,3$ and $\nu=3,4$.

different number of shells. The results thus obtained are compared with other theoretical calculations. As it is seen from these tables the contribution of the second shell is very essential, but decreases with increasing the number of level v. The analysis of Tables IV and V confirms the conclusion, made for DES of H^-, about the conver-

gence of the HSA expansion for DES, though the rate of convergence for He is somewhat lower than H^-. Nevertheless, the results of calculations of He DES in the HSA approach show that it is sufficient to use a small number (≤ 4) of radial equations to get a required accuracy ($\sim 10^{-4}$ a.u.). It is seen from Tables IV and V that our results are in perfect agreement with the best variational calculations [20–22] and with the 20-state close-coupling method with pseudostates [23] which provide the most exact values of DES energies.

The high rate of convergence of the HSA expansion and the correct and natural way of taking into account the electron correlations make the coupled-channel HSA approach very attractive for carrying out systematic calculations of spectral characteristics of two-electron systems. It would also be interesting to apply the multichannel HSA approach to study the nonadiabatic effects on the widths of autoionizing states and photoionization cross sections of heliumlike systems.

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