# Analysis of Triply Excited States of Atoms in Hyperspherical Coordinates

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A new method for obtaining accurate adiabatic potential curves of a three-electron atom in hyperspherical coordinates has been developed. These potential curves are used to study singly, doubly, and triply excited states all at the same time. The group of potential curves that supports triply excited states of atoms is analyzed. For the Li atom, these curves are used to interpret and identify the triply excited states observed recently in the measurements using synchrotron radiation. For the $H^{2-}$ ion, all the potential curves are repulsive, which clearly implies that there are no resonances of any type for this system.

Triply excited states of atoms and ions are examples of "hollow atoms" which are formed in ion-surface collisions [1] as well as in electron impact ionization of positive ions [2]. In these experiments the energy resolution is often not high enough to resolve individual states, thus the nature of hollow atoms has not been examined carefully so far. Recently numerous resonances of Li atoms have been observed using synchrotron radiation light sources by Azuma *et al.* [3], following the earlier photoabsorption experiment [4]. These resonances lie in the energy region where they can be attributed to triply excited states of Li. This has been a subject of considerable interest recently [5] and other experiments are under way [6].

Multiply excited states of a microscopic system cannot be described using the independent particle approximation. The study of doubly excited states of atoms in the past decades has shown that many new features such as the supermultiplet structure of energy levels and the regularity in autoionization widths of doubly excited states are best described using new theoretical approaches which treat the joint motion of the two electrons directly [7]. One of these successful methods is the hyperspherical approach which can provide not only the classification of doubly excited states but also a computational method for obtaining accurate atomic photoionization cross sections and resonance parameters [8].

This Letter reports the first accurate results in extending the hyperspherical approach to three-electron systems to examine the properties of triply excited states. Although the hyperspherical approach for three-electron systems has been discussed previously [9], these early works employed a number of approximations and did not give sufficient numerical accuracy to make quantitative predictions. Based on a recent formulation of three-electron atoms in hyperspherical coordinates [10], we have now calculated accurate adiabatic potential curves of the Li atom in the $^2P^o$ symmetry. The nine adiabatic potential curves that converge to the $2l2l'$ manifolds of the $Li^+$ ion are used to obtain approximate eigenenergies which allow us to iden-

tify the resonances observed by Azuma *et al.* [3]. We have also calculated the corresponding adiabatic potential curves for $H^{2-}$ ions to examine the possible existence of resonances in this system.

For a three-electron atomic system, the hyperspherical coordinates are obtained by replacing the radial distances of the three electrons, $r_1$, $r_2$, and $r_3$, by a hyperradius $R$, and two hyperangles $\alpha_1$ and $\alpha_2$, defined by $r_1 = R \sin\alpha_1 \cos\alpha_2$, $r_2 = R \sin\alpha_1 \sin\alpha_2$, and $r_3 = R \cos\alpha_1$, where $0 \le R \le \infty$ and $0 \le \alpha_1, \alpha_2 \le \pi/2$. The other coordinates are the spherical angles of each electron.

The total wave function is solved in the adiabatic expansion method, $\psi = \sum_\mu F_\mu(R)\Phi_\mu(R;\Omega)$, where $\Omega$ is the set of all angles and the spins. The channel function $\Phi_\mu(R;\Omega)$ is the solution of the Schrödinger equation at fixed values of $R$,

$$H|_{R=\text{const}}\Phi_\mu(R;\Omega) = U_\mu(R)\Phi_\mu(R;\Omega), \qquad (1)$$

with $\mu$ being a channel index. The partial differential equation (1) above still involves eight spatial variables and the solutions are required to satisfy permutation symmetry when any pair of electrons are interchanged. To reduce the dimensionality in the calculation, we first expand $\Phi_\mu(R;\Omega)$ in terms of spherical harmonics for each electron. These spherical harmonics with fixed $(l_1, l_2, l_3)$ are coupled with the spins to form proper total orbital and spin angular momenta and parity, as well as exchange symmetry. Within this subspace Eq. (1) can then be reduced to a set of coupled two-dimensional partial differential equations which are solved using the *B*-spline technique [11]. The final adiabatic potential curves are obtained after including the coupling among selective groups of $(l_1, l_2, l_3)$ which are important for the problem under study. In the present calculation we focus on the $^2P^o$ triply excited states of Li which are reached by single photoabsorption from the $^2S^e$ ground state. We will concentrate on the group of states that lie below the $2l2l'$ states of $Li^+$. Thus the $(l_1, l_2, l_3)$ groups included to

assure convergence in the calculation are (0,0,1), (1,1,1), (0,1,2), and (1,1,3).

Figure 1(a) shows the adiabatic potential curves for $^2P^o$ states of Li. They can be divided into three groups. The first group consists of the lowest potential curve. It approaches the $1s^2\,^1S^e$ limit of Li$^+$ at large $R$, and this potential curve supports all the $1s^2np\,^2P^o$ singly excited states of Li. The second group of potential curves supports doubly excited states of Li. For example, the next six lowest potential curves support doubly excited states of $1s2lnl'\,^2P^o$ type, and their four asymptotic limits are $1s2s\,^1S^e$, $1s2s\,^3S^e$, $1s2p\,^3P^o$, and $1s2p\,^1P^o$ of Li$^+$. Notice that there are two curves approaching each $1s2p^{1,3}P^o$ limit, one from (0,0,1) and the other from (0,1,2). The higher members of the second group support doubly excited states of the types $1s3lnl'$, $1s4lnl'$, etc. In Fig. 1(a) all the triply excited states are supported by the uppermost group of potential curves. These curves are redrawn in more detail in Fig. 1(b).

Figure 1(b) shows that the potential curves that support triply excited states have numerous avoided crossings with the higher members of the potential curves that support doubly excited states. These avoided crossings are rather sharp and are treated as diabatic crossings in the first order approximation considered here. The resulting final lowest nine potential curves of this third group are shown in Fig. 2(a) where we allow some of the curves to undergo diabatic crossing if the avoided crossing between the two nearby curves is sharp. This is an approximation adopted for the present in order to analyze the triply excited states that are supported by these potential curves. Future accurate calculations similar to the hyperspherical close coupling method for two-electron atoms would allow us to remove these restrictions.

The nine potential curves in Fig. 2(a) support nine Rydberg series of the type $2l2l'nl''\,^2P^o$. Each Rydberg series converges to one of the six different doubly excited states of Li$^+$, namely, $2s^2\,^1S^e$, $2s2p\,^3P^o$, $2p^2\,^3P^e$, $2p^2\,^1D^e$, $2s2p\,^1P^o$, and $2p^2\,^1S^e$, if conventional approximate single particle configurations are used for these doubly excited states. In Fig. 2(b) we show the resonances observed by Azuma *et al.* [3]. The triply excited states belonging to this energy region are labeled as $A, B, \ldots, K$ by these authors, for lack of a more suitable designation.

The hyperspherical potential curves shown in Fig. 2(a) allow us to estimate the energy levels of triply excited states. By using the adiabatic approximation, i.e., ignoring the coupling between channels, we solve the eigenvalues of the first few lower states from each potential curve. The results are listed in Table I where they are also compared with the experimental values and those obtained by multiconfiguration Dirac-Fock (MCDF) calculations
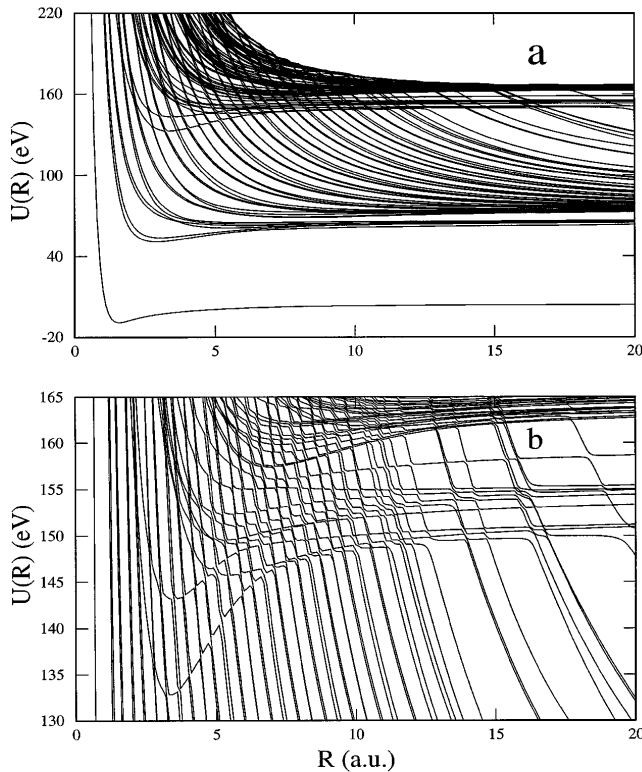


FIG. 1. (a) The hyperspherical potential curves for the $^2P^o$ states of lithium atom as a function of $R$. The energy is measured from the ground state ($E_0 = 203.4283$ eV). (b) Potential curves that support triply excited states are shown in an expanded scale.
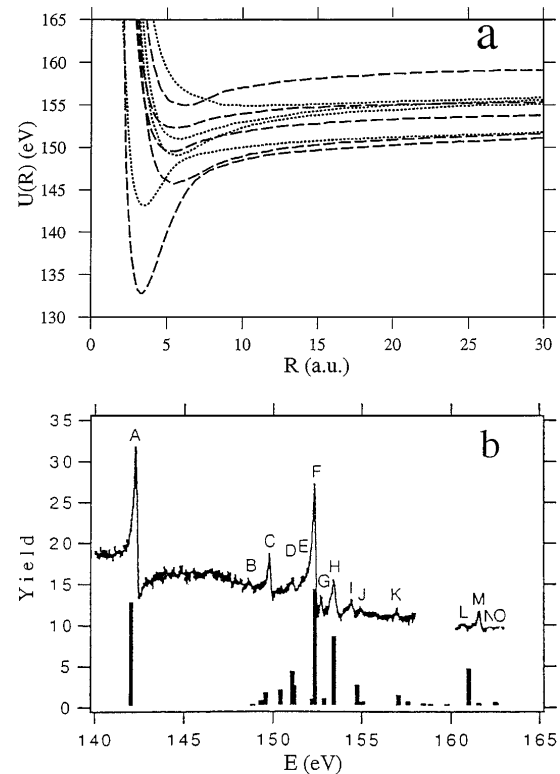


FIG. 2. (a) The $^2P^o$ potential curves that converge to the $2l2l'$ manifold of Li$^+$ as a function of $R$. (b) The experimental spectra of triply excited states of Li and the resonance positions obtained from the MCDF calculation (from Ref. [3]).

TABLE I. Energy positions of triply excited states for Li. Data from experiment and from multiconfiguration Dirac-Fock calculations (with a shift of 0.4 eV upward) are from Ref. [3]. The hyperspherical channels are ordered by the minimum values of their potential curves.

| | Expt. (eV) | MCDF (eV) | Eigenvalues of hyperspherical channels (eV) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th | 9th |
| A | 142.35 | 141.657 | 141.23 | | | | | | | |
| B | 148.7 | 148.439, 148.92, 149.187 | | 148.60 | 148.56 | | | | | |
| C | 149.79 | 150.008 | 149.02 | | | | | | | |
| D | 151.10 | 150.665, 150.789 | 150.45 | 151.02 | 150.80 | | | | | |
| E | 151.7 | 151.805 | 151.00 | 151.67 | 151.56 | | | | | |
| F | 152.32 | 151.955 | | | | | 151.89 | | | |
| G | 152.72 | 152.47 | | | | 151.92 | | | | |
| H | 153.43 | 153.042 | | | | | 153.41 | 153.21 | | |
| I | 154.43 | 154.32 | | | | 154.29 | 153.97 | | 154.22 | |
| J | 155.0 | 154.668 | | | | 155.14 | | 154.93 | 155.24 | |
| K | 157.0 | 156.644, 157.176 | | | | | | | | 157.12 |

reported in Ref. [3]. The eigenvalues from each potential curve are then used to identify and group the experimentally observed resonances. Note that we number the curves according to the value of the potential minimum of each curve, with the lowest one being the first curve.

From the calculation, it is clear that the $A$ and $C$ resonances belong to the first potential curve. In the experiment they have similar shapes as they should if both belong to the same series. Resonance $A$ has been denoted as the $2s^2 2p\,^2P^o$ state and has been studied in many experiments [3–5]. Two states have been assigned to the $B$ resonance in the experiment. They are the lowest state of each of the second and third curves of Fig. 2(a). The $B$ resonance has very small intensity. This is understood from the fact that these two potential curves have small $(l_1, l_2, l_3) = (0, 0, 1)$ angular momentum components at small $R$. In a single photon absorption process from the $1s^2 2s\,^2S^e$ ground state of Li which has mostly $(l_1, l_2, l_3) = (0, 0, 0)$, the one-electron dipole transition operator can change only one unit of orbital angular momentum and thus a small $(l_1, l_2, l_3) = (0, 0, 1)$ component in the channel function would result in weak oscillator strength. The $D$ and $E$ resonances in the experiment are assigned to be the excited states of the first three potential curves. They have smaller oscillator strengths due to the typical $1/n^3$ rule ($n$ being the principal quantum number of the outermost electron) for the oscillator strengths of excited states within a given series. Since the first member of the 2nd and 3rd curves has small intensities already, the observed strengths of the $D$ and $E$ resonances are most likely from the 3rd and 4th states of the first curve.

In the experimental data the $F$, $G$, $H$, and $I$ resonances are rather broad. They also have non-negligible oscillator strengths. They are identified as the lowest member of each of the 5th, 4th, 6th, and 7th potential curves in Fig. 2(a). These curves converge to the higher energy thresholds in the asymptotic region (large $R$) and thus can autoionize to the lower doubly excited states of the same manifold. Since the autoionized electron has small energy in such transitions, the autoionization rates are large, thus explaining the broader widths of these states. That oscillator strengths of these states are somewhat larger (especially when compared to $B$) is explained by the fact that the composition of these higher potential curves has larger $(l_1, l_2, l_3) = (0, 0, 1)$ components. The calculations also show that the 2nd and 3rd states of the 5th curve are near the observed $H$ and $I$ resonances, respectively. Since the first member of this series, the $F$ resonance, is so pronounced, we cannot rule out significant contributions of these excited states in the observed $H$ and $I$ resonances.

There are several candidates for the experimental $J$ resonance, as listed in Table I, and its intensity is probably coming from more than one state. The $K$ resonance is assigned to the lowest state of the 9th potential curve. This curve has a large angular momentum component $(l_1, l_2, l_3) = (1, 1, 1)$, and the oscillator strengths of its eigenstates are weak. The 8th potential curve, the highest one in this manifold at small $R$, consists mostly of high angular momentum components $(l_1, l_2, l_3) = (1, 1, 3)$ and is repulsive in the region of $R < 15$. It has a very shallow well in the large $R$ region and there is no indication that its eigenstates are populated. (Note that its lowest state would be called $2p^2 4f$ in the independent particle picture.) The four states labeled $L$, $M$, $N$, and $O$ in Fig. 2(b) are triply excited states associated with the $2l3l'$ limits of $Li^+$ and are not analyzed here.

The above analysis indicates that the calculated hyperspherical potential curves allow us to make a semiquantitative interpretation of the observed triply excited states. So far we can only associate the resonances to particular individual potential curves. It would be desirable to assign a new set of quantum numbers for these curves. However, with 5 internal degrees of freedom (two hyperangles and three $\theta_{ij}$ angles between each pair of electrons with respect to the nucleus) the search for new quantum numbers is a task for the future after triply excited states of different

symmetries are examined. In this respect we could say that the present status for the understanding of triply excited states is about the same as the situation of doubly excited states in 1968 when doubly excited states were first identified with adiabatic hyperspherical potential curves [12]. We should mention that other theoretical approaches are capable of obtaining accurate positions and widths of triply excited states, like the $R$-matrix method [13] or the multi-configuration interaction method [14]. However, the hyperspherical approach provides a method for separating the observed "irregular" spectra into different channels in a first order approximation. Accurate results where channel interaction and the autoionization of these states are included can be achieved by using the hyperspherical close coupling method [8] in the future.

As a by-product, we also calculated the $^2P^o$ potential curves for $H^{2-}$. Earlier experiments [15,16] claimed to have observed resonances in this system for electron energies at 14.5 and 17.2 eV in the collision of $e^- + H^- \rightarrow e^- + e^- + H$. These "resonances" are above the total breakup threshold (0.75 + 13.6 eV) and they were "identified" to have the $2s^2 2p\, ^2P^o$ and $2p^3\, ^2P^o$ configurations by Ref. [17]. The existence of such resonances above the total breakup threshold has been questioned by Robicheaux et al. [18]. They performed a more detailed $R$-matrix calculation but failed to find the claimed resonances. The recent experimental study of $e^- + D^-$ collisions using the storage ring in Aarhus [19] also failed to find any resonances for this system. While there is no reason for us to believe that these resonances should exist, it is always possible to argue that there may be some narrow resonances which have been overlooked in the calculation or in the experiment when the electron energy is scanned. To put such possible speculation to rest, we calculated the adiabatic potential curves for the $H^{2-}$ system with the $^2P^o$ symmetry. (Recall that the resonances claimed in the calculations of Ref. [17] belong to this symmetry.) All the potential curves calculated were repulsive. The most likely places where such resonances could have existed

would be the triply excited states. In Fig. 3 we show the first five potential curves of the $^2P^o$ symmetry of $H^{2-}$ that would have supported the triply excited states. Note that the potential curves are repulsive for all values of $R$ and there are no indications of any potential wells. This clearly indicates that there are no resonances of any kind for the $H^{2-}$ system.

In summary, we have obtained accurate hyperspherical potential curves for the $^2P^o$ symmetry of Li to analyze the recently observed triply excited states. It is shown that we can associate the observed states with the calculated adiabatic potential curves and identify states that belong to the same series. We have also obtained hyperspherical potential curves for $H^{2-}$. The potential curves are all repulsive and we conclude that there are no resonances of any kind for this system.

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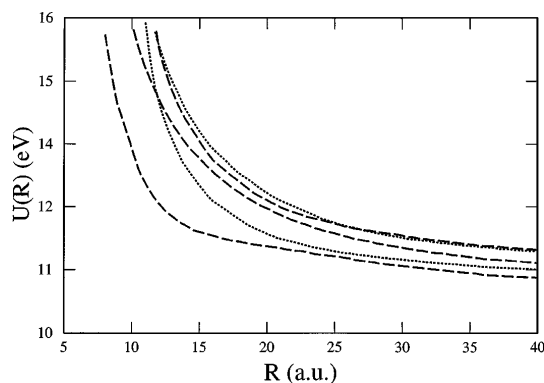[19] L. H. Andersen et al., Phys. Rev. Lett. **74**, 892 (1995).

FIG. 3. The five lowest $2P^o$ potential curves of $H^{2-}$ measured from the ground state of $H^-$ that converge to the $2l2l'$ manifold of $H^-$ as a function of $R$.