

Exponentially correlated Hylleraas-configuration interaction studies of atomic systems. II. Non-relativistic energies of the 1^1S through 6^1S states of the Li^+ ion

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Abstract

The exponentially correlated Hylleraas-configuration interaction wave function (E-Hy-CI) is a generalization of the Hylleraas-configuration interaction (Hy-CI) in which the single r_{ij} of an Hy-CI wave function is generalized to the generic type $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$. This type of correlation has the right behavior both in the vicinity of the r_{ij} cusp and as r_{ij} goes to infinity; this work shows that wave functions containing both linear and exponential r_{ij} factors converge more rapidly than either one alone for low-lying excited states of 1S symmetry. E-Hy-CI variational calculations with up to 8568 configurations lead to a nonrelativistic energy of $-7.2799\ 1341\ 2669\ 3059\ 6491\ 6759$ hartree for the 1^1S ground state of the Li^+ ion.

KEYWORDS

correlated wave functions, E-Hy-CI, exponentially correlated Hylleraas-configuration interaction, Li^+ states

1 | INTRODUCTION

Variational methods based on explicitly correlated wave functions are known to give the most precise upper bounds to energy states, and hence the inclusion of terms containing the interelectronic distance r_{ij} in the wave function has become increasingly common, at least for few-electron atomic systems ($N \leq 4$) (so common in fact that a book dealing entirely with explicitly correlated wave functions has been produced [1]; for a recent article see Grüneis et al. [2]). Wave functions that are commonly referred to now as Hylleraas (Hy) follow the landmark calculation of Hylleraas [3] by employing powers of the interelectronic distance in the wave function. The Hylleraas-configuration interaction (Hy-CI) technique (developed by Sims and Hagstrom (SH) [4] and also independently by Woźnicki [5]) differs from the traditional Hy development by employing at most a single, linear r_{ij} factor with traditional CI orbital bases in each configuration state function (CSF). While the work of Hylleraas demonstrated that two-electron atoms could be calculated precisely (for that time) with powers of r_{12} , it was Bunge [6] who demonstrated that linear terms alone were sufficient for high precision for He^1 . Hy-CI in its current incarnation utilizes only linear terms in r_{ij} , hence R12/F12 [1, 2, 9, 10] methods are related to Hy-CI but outside the scope of this study (but see Ruiz [11] for a discussion of CI-R12 and a comparison with Hy-CI in the two-electron He atom case). In an interesting new development, Nakashima and Nakatsuji have introduced Hy-CI into their free-complement chemical formula theory (FC-CFT) [12–15]. The other common exponentially correlated wave function, the exponentially correlated Gaussian (ECG) [1] wave function, in contrast to Hy and Hy-CI wave functions has the r_{ij} correlation appearing as Gaussian exponentials.

In this paper we continue to explore² a generalization of the Hy-CI method first proposed by Wang et al. [16], the Exponentially correlated Hylleraas-configuration interaction (E-Hy-CI) method³ in which the single r_{ij} of an Hy-CI wave function is generalized to a form of the generic type $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$. Pairing an exponential r_{12} factor with linear r_{12} was first suggested for helium by Hirschfelder who, in 1960 [17], suggested that this type of correlation factor has the right behavior in the vicinity of the r_{12} cusp, and also has the right behavior as r_{12} goes to infinity, but he did no calculations. Whether functions having both linear and exponential r_{ij} factors might be more rapidly convergent than either one alone remained to be seen. The E-Hy-CI proposal has been followed by many papers discussing the integrals arising in E-Hy-CI [16–21], but there had been no atomic

or molecular structure E-Hy-Cl calculations other than an examination of optimized values of ω_{ij} for the E-Hy-Cl wave function by Nakatsuji (which is referred to as unpublished in Wang et al. [16]) until our recent study [7] of the ground 1^1S state of the helium atom. The present contribution continues that work on the ground 1^1S state of the helium atom by examining not only the ground 1^1S state of the Li^+ ion, but the 2^1S through 6^1S excited states as well, comparing our present results with Hy-Cl calculations [22] of these states.⁴

2 | VARIATIONAL CALCULATIONS

For N_e electrons, the total non-relativistic, stationary-point-nucleus energy E_{NR} is defined as the exact solution (eigenvalue) of the time-independent, non-relativistic Schrödinger equation

$$H_{NR}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}) = E_{NR}\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e}), \quad (1)$$

where the Hamiltonian H_{NR} is defined as (in atomic units)

$$H_{NR} = \sum_{i=1}^{N_e} \mathcal{H}_i + \sum_{i < j}^{N_e} r_{ij}^{-1}. \quad (2)$$

Here $\mathcal{H}_i = \mathcal{T}_i + \mathcal{V}_i$, \mathcal{H}_i being a one-electron operator (electron i) consisting of a kinetic energy part $\mathcal{T}_i = -\frac{1}{2}\nabla_i^2$ and a nuclear attraction part $\mathcal{V}_i = -Z/r_i$. N_e denotes the number of electrons and Z the corresponding nuclear charge. How $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})$ in Equation (1) is constructed to be an E-Hy-Cl wave function with the correct symmetry for the atomic states of interest (including being antisymmetric to satisfy the Pauli exclusion principle) is discussed in this and the next section.

The E-Hy-Cl wave function for N_e electron atomic states is

$$\Psi = \sum_{K=1}^N C_K \Phi_K, \quad (3)$$

where

$$\Phi_K = \Lambda \left(r_{ij}^{\nu_K} e^{-\omega_K r_{ij}} \prod_{s=1}^{N_e} \{ \phi_{K_s}(\mathbf{r}_s) \} \Theta_K \right) = O_{as} O_{L, M_L} O_{S, M_S} \left(r_{ij}^{\nu_K} e^{-\omega_K r_{ij}} \prod_{s=1}^{N_e} \{ \phi_{K_s}(\mathbf{r}_s) \} \Theta_K \right) \quad (4)$$

denotes the K^{th} antisymmetrized spin and angular momentum projected explicitly correlated CSF. Λ is the symmetry adaptation operator which does the projection and is a product of a projection operator which makes the state antisymmetric, O_{as} , and O_{L, M_L} , O_{S, M_S} which are idempotent orbital and spin angular momentum projection operators of the Löwdin type [24] for a state of total quantum numbers L, M_L, S, M_S (Russell-Saunders [LS] coupling is assumed). The idempotent antisymmetry projection operator O_{as} is given by

$$N_e! O_{as} = \sum_P (-1)^P P \quad (5)$$

where the summation runs over all the $N_e!$ permutations P , with p being the parity of the corresponding permutation P . Each term K contains at most one explicitly correlated factor $r_{ij}^{\nu_K} e^{-\omega_K r_{ij}}$ which in addition to the Hy-Cl case with $\omega_K = 0$ can also have $\omega_K \neq 0$. In practice it is sufficient to take ν_K equal to 0 or 1, with $\nu_K = 1$, $\omega_K = 0$ the Hy-Cl case and $\nu_K = 0$, $\omega_K = 0$ the CI case. Θ_K is a primitive spin product function for term K and $\phi_{K_s}(\mathbf{r}_s)$ represents the s^{th} basis orbital in the K^{th} term.

The basis orbitals are un-normalized Slater-type orbitals (STOs) $\phi(\mathbf{r})$ which are defined as

$$\phi_i(\mathbf{r}) = [n_i, l_i, m_i]_{\xi_i} = r^{n_i-1} e^{-\xi_i r} Y_{l_i}^{m_i}(\theta, \phi), \quad (6)$$

where $Y_l^m(\theta, \phi)$ is a normalized spherical harmonic in the Condon and Shortley phase convention [25]. With this choice of phase convention, the spherical harmonics satisfy

$$Y_I^{m*}(\theta, \phi) = (-1)^m Y_I^{-m}(\theta, \phi). \quad (7)$$

The coefficients C_K in Equation (3) are found in this work by solving the generalized eigenvalue problem

$$\mathbf{HC} = E\mathbf{SC}, \quad (8)$$

$$(\mathbf{H} - E_0\mathbf{S})\mathbf{C} = (E - E_0)\mathbf{SC}, \quad (9)$$

$$\mathbf{C} = (E - E_0)(\mathbf{H} - E_0\mathbf{S})^{-1}\mathbf{SC}, \quad (10)$$

where the matrix elements are given by $\mathcal{H}_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle$ and $S_{KL} = \langle \Phi_K | \Phi_L \rangle$ with the Hamiltonian H given by Equation (2) and E_0 is some starting approximation for the eigenvalue E of interest.

The details of how the authors solve this real symmetric-definite eigenvalue problem are discussed in Sims and Ruiz [26], including how to obtain a quadruple precision version of our computationally fast Fortran 90+ portable parallel package suitable for large (80 000 x 80 000 or greater) dense matrices. All results reported in this article were obtained using real*32 extended precision (quad-double-with exponent or QDE, 256-bit, ≈ 64 digits) floating point arithmetic, and the Message Passing Interface (MPI) Standard [27] was used to parallelize the code.

3 | METHOD OF CALCULATION

For two electrons, following Hy-Cl [28] spin can be eliminated and the E-Hy-Cl wave function becomes:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{K=1}^N C_K \Phi_K(\mathbf{r}_1, \mathbf{r}_2), \quad (11)$$

where the terms Φ_K are specifically of the form

$$\Phi_K(\mathbf{r}_1, \mathbf{r}_2) = r_{12}^{\nu_K} e^{-\omega_K r_{12}} (1 \pm P_{12}) O_{L, M_L}(\phi_{K_1}(\mathbf{r}_1) \phi_{K_2}(\mathbf{r}_2)). \quad (12)$$

P_{12} is the operator which permutes electrons 1 and 2, and the plus sign is for singlet levels, the minus sign for triplet levels. Equation (2) becomes

$$H_{NR} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{12}, \quad (13)$$

where $\mathcal{H}_{12} = r_{12}^{-1}$.

In the generalized eigenvalue problem $\mathbf{HC} = \lambda\mathbf{SC}$, matrix element H_{KL} is

$$H_{KL} = \langle \Phi_K | \mathcal{H} | \Phi_L \rangle = \langle \Lambda \Phi_K^p | \mathcal{H} | \Lambda \Phi_L^p \rangle, \quad (14)$$

where Φ_K^p denotes the K th primitive (unprojected) function as given in Equation (4) above. S_{KL} is similar, with \mathcal{H} replaced by the unit operator 1.

The projection reduction of these matrix elements is same projection reduction used in lithium [29] and in beryllium [30] and is discussed in appendix A of those references. The helium case is simpler so just the result is given here, which is that H_{KL} is given by

$$H_{KL} = \langle g_K f_K | \mathcal{H} | O_{L, M_L} B(g_L f_L) \rangle. \quad (15)$$

In Equation (15) one can apply O_{L, M_L} either before or after applying $B = 1 + P_{12}$. Here the permutations B are applied to $g_L f_L$ first, then the O_{L, M_L} projection is done on the resultant. The O_{L, M_L} projection is applied only on the orbital products since $g_L = r_{ij}^{\nu_L}$ commutes with O_{L, M_L} [4].

Now to generalize Hy-Cl to E-Hy-Cl for the two electron He case, one merely has to take the correlation factor g_K to be $g_K = r_{ij}^{\nu_K} e^{-\omega_K r_{12}}$ in the formulas above since $e^{-\omega_K r_{12}}$ has the same symmetry properties as r_{12} . Thus H_{KL} becomes

$$H_{KL} = \langle \phi_{K_1}(\mathbf{r}_1) \phi_{K_2}(\mathbf{r}_2) r_{12}^{\nu_K} e^{-\omega_K r_{12}} | \mathcal{H} | r_{12}^{\nu_L} e^{-\omega_L r_{12}} (1 + P_{12}) O_{L, M_L} \phi_{L_1}(\mathbf{r}_1) \phi_{L_2}(\mathbf{r}_2) \rangle. \quad (16)$$

A detailed discussion of the most general exponentially correlated integrals which have to be evaluated when using this wave function can be found in section 3 of our recent study [7] of the ground state of helium.⁵

4 | COMPARISON OF E-HY-CI AND HY-CI

4.1 | Basis sets and optimization of the orbital exponents

The basis set orbitals in Hy-CI atomic calculations are STOs, see Equation (6). For the nonlinear orbital exponent parameters, there are essentially four distinct approaches to be employed. The first approach is to work with a fixed set of orbital exponents. The fixed exponents have been previously optimized in a shorter expansion, corresponding to an outer region. Examples of this type of optimization are given in [31, 32]. This is the approach favored by one of the authors (Ruiz [11, 22]); for two electron systems only a single orbital exponent is used and this exponent is optimized. The second method consists of optimizing the exponents of the orbitals for each term as a term is added, and then recycle a subset of the basis set and reoptimize the exponents one basis function at a time. In this procedure there are different orbital exponents for each term, leading to a rather large number of orbital exponents to be optimized, a very computationally expensive task. An example of the use of this method is the calculation of King and Bergsbaken [33]. The third approach is due to Drake [34, 35], who pointed out the need for ‘doubling’ basis sets so there is a natural partition of the basis set into two distinct distance scales—one appropriate to the complex correlated motion near the nucleus, and the other appropriate further out.⁶ The fourth approach is the one employed by Sims and Hagstrom in their He calculations in 2002 [28]. Drake [34, 35] uses just two sets of orbitals to accelerate convergence, the Sims and Hagstrom approach uses two sets of basis functions for each l , differing in the nonlinear parameters ξ and ξ' .

In paper I [7] of this series, we explored what might be thought of as a synthesis of the Ruiz (single orbital exponent ξ) and Sims and Hagstrom (two orbital exponents, ξ and ξ' for each l) procedures by using just two orbital exponents (ξ and ξ') in a calculation on the He ground $1S$ state. That work is continued here in a calculation of ground and excited states of the Li^+ ion. Frolov and Ruiz (FR) [22] used the Ruiz single (orbital exponent) basis set in their Li^+ Hy-CI calculations. In the ‘doubled’ (orbital exponent) basis set Hy-CI introduced in paper I and continued here, the first set has an orbital with an orbital exponent ξ that makes it essentially a valence shell orbital similar to the Ruiz outer (valence) shell orbital, whereas for the second set, the orbital has a large exponent ξ' which brings it in closer to the nucleus. Results are very good for the ground state; here we also explore how well this works for excited states.

4.2 | E-Hy-CI using single and “doubled” exponential r_{12} factors

To clarify this further, consider Table 1, where single and “doubled” basis sets for the Hy-CI calculations are listed (Table 2 will list basis sets for E-Hy-CI calculations as well). Each line in the table specifies the {outer,outer} or {inner,inner} and {outer,outer} sets for each l quantum number ($=l_{\max}$). In the table, only the minimum information needed to specify the basis set is listed, namely, an exponent ξ , the l quantum number for orbitals with that exponent, and n_{orbs} , the number of orbitals with that exponent (the n_i in Equation (6) run from $l_i + 1$ to $l_i + n_{\text{orbs}}$). ω_{12} , the exponent of the exponentially correlated r_{12} factor if this is an E-Hy-CI calculation, is not included in this table since these are Hy-CI calculations, but will be included in subsequent tables. There is of course just one n_{orbs} for the single (orbital exponent) basis set Hy-CI calculations and an outer n_{orbs} and inner n'_{orbs} basis set for ‘doubled’ basis sets. In all of the tables, N is used to refer to the number of terms in the wave function (see Equation 3).

In Table 1 we start out with the FR [22] 820 term $[16s14p13d12f]$,⁷ $\xi = 2.520933$ wave function and extend it to 974 terms $[18s15p14d13f]$. Since $\xi = 2.9814$ was the optimized single ξ for a comparable basis set for He [11], we also used this orbital exponent as well as the exponent, $\xi = 4.4721$, obtained by a simple nuclear charge based scaling of the He wave function (which in this case means to scale the orbital exponent by a factor of 3.0/2.0). We still are not at a minimum, so one more calculation at $\xi = 5.9628$ provided enough points to fit a smooth curve and yield an optimized single orbital exponent of $\xi = 5.2424$.

Next we doubled the basis set by including the {inner,inner} set as well. Optimizing ξ' yields a $\xi' = 16.93$ which reduces the energy error from ≈ 5 nanohartree (FR) to ≈ 2 picohartree. The 1482 term result is intended to give an indication of the limit for a single basis set $l_{\max} = 3, s, p, d, f$ Hy-CI for ground $1S Li^+$. In Table 2 we include both the {inner,inner} and {outer,outer} terms which were key to the success of the current Hy-CI formalism in the 2002 study [28], and examine whether the use of different orbital exponents for different l quantum numbers can be simplified by the use of a just two orbital exponents, one for the {inner,inner} set and one for the {outer,outer} set. The table includes the SH 4284 term l -wave expansion for Li^+ , 18 decimal place precision. This expansion was obtained, as mentioned above, from simple nuclear charge based scaling of a He wave function which was obtained by meticulously optimizing the {outer,outer} and {inner,inner} orbital exponents for each l value in

TABLE 1 Comparison of theoretical Hy-Cl energies for the Li^+ ground state using a single basis set of orbitals (one ξ), and a “doubled” basis set of orbitals (one ξ , one ξ')

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	N	Energy (hartree)
Hy-Cl	This work	0	18	2.5209 33 ^a			342	-7.2795 3375 8749 7051 0936 6440
Hy-Cl	This work	0	18	4.4721			342	-7.2795 3506 4023 8622 6088 4297
Hy-Cl	This work	1	15	2.5209 33			582	-7.2799 1314 7044 7679 0886 1385
Hy-Cl	This work	1	15	4.4721			582	-7.2799 1316 0636 0229 7610 7764
Hy-Cl	This work	2	14	2.5209 33			792	-7.2799 1340 9842 1134 8060 2734
Hy-Cl	This work	2	14	4.4721			792	-7.2799 1341 2406 3723 2211 2329
Hy-Cl	This work	3	13	2.5209 33			974	-7.2799 1341 0126 1638 0754 7317
Hy-Cl	This work	3	13	4.4721			974	-7.2799 1341 2634 6416 7046 8968
Hy-Cl	FR (2010) [22]	3	16 ^b	2.5209 33			820	-7.2799 1340 746
Hy-Cl	This work	3	18 ^c	2.5209 33			974	-7.2799 1341 0126 1638 0754 7317
Hy-Cl	This work	3	18	2.9814			974	-7.2799 1341 1941 4309 4089 3918
Hy-Cl	This work	3	18	4.4721			974	-7.2799 1341 2634 6416 7046 8968
Hy-Cl	This work	3	18	5.2424			974	-7.2799 1341 2658 9150 6525 5767
Hy-Cl	This work	3	18	5.9628			974	-7.2799 1341 2651 6353 1849 6768
Hy-Cl	This work	3	19 ^d	5.2424			1482	-7.2799 1341 2662 9081 2013 3837
Hy-Cl	This work	3	18	5.2424	18	15.50	1948	-7.2799 1341 2669 1060 7823 3099
Hy-Cl	This work	3	18	5.2424	18	16.93	1948	-7.2799 1341 2669 1062 1481 4476
Hy-Cl	This work	3	18	5.2424	18	20.50	1948	-7.2799 1341 2669 1053 6411 2505
Hy-Cl	This work	3	18	5.2424	18	40.50	1948	-7.2799 1341 2669 0691 2688 6261
Reference ^e								-7.2799 1341 2669 3059 6491 9459

Note: All energies are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^aThe exponent is from Frolov and Ruiz [22].

^b16 here represents $n_{\text{orbs}} = 16, 14, 13,$ and $12,$ respectively for $l = 0-3.$

^c18 here and below represents $n_{\text{orbs}} = 18, 15, 14$ and $13,$ respectively for $l = 0-3.$

^d19 here represents $n_{\text{orbs}} = 19, 19, 19$ and $18,$ respectively for $l = 0-3.$

^eNakatsuji and Nakashima [38].

succession. Also included is our expansion, obtained from the same l -wave expansion, but using just the two “doubled” basis set exponents obtained previously.

4.3 | E-Hy-Cl versus Hy-Cl using a different ‘doubled’ basis set for each different l -wave

Including both {inner,inner} and {outer,outer} terms was key to the success of the current Hy-Cl formalism in the 2002 study [28]. The effect of converting those ‘doubled’ basis set Hy-Cl wave functions into “doubled” basis set E-Hy-Cl wave functions is explored in this section using the same simple procedure used in paper I: for each term in the wave function, add to the wave function a term now also containing an exponentially correlated $e^{-\omega_{12}r_{12}}$ factor whose exponent ω_{12} is chosen to be the same 0.5 which satisfies the Kato cusp condition (here also scaled by the nuclear charge based scaling of $3.0/2.0,$ i.e., we choose $\omega_{12} = 0.75$). The results are tabulated in Table 2, where very dramatic improvements can be seen:

- Hy-Cl s -wave 3 decimal place precision becomes 6 decimal place E-Hy-Cl s -wave precision ($>$ Hy-Cl p -wave precision),
- Hy-Cl p -wave 6 decimal place precision becomes 12 decimal place E-Hy-Cl p -wave precision ($>$ Hy-Cl f -wave precision),
- Hy-Cl d -wave 9 decimal place precision becomes 18 decimal place E-Hy-Cl d -wave precision ($>$ Hy-Cl g -wave precision), a huge 9 decimal place improvement,
- From here on, convergence gets slower, but already at the E-Hy-Cl d -wave expansion, the result is almost as good as the Hy-Cl $l = 6$ result.

It is clear from the Table 2 results that the SH 18 decimal place $l = 6$ Hy-Cl result can be improved on with just an $l = 3$ E-Hy-Cl basis. It is also clear that while optimizing each l -wave orbital exponents separately achieves the better results, as is to be expected (the best E-Hy-Cl result being 21 decimal digit precision), 16 decimal digit precision can be obtained with just an s,p,d,f basis and just two ξ, ξ' exponents.

TABLE 2 Comparison of theoretical E-Hy-Cl and Hy-Cl energies for the Li^+ ground state using a “doubled” basis set of orbitals (one ξ , one ξ') and a “doubled” basis set of orbitals for each l -wave

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-Cl	This work	0	19	5.2424	19	16.93		760	-7.2795 3550 6348 5151 8152 0384
Hy-Cl	SH (2002) [28]	0	19	3.30	19	37.50		760	-7.2795 3549 6974 7375 7655 4093
E-Hy-Cl	This work	0	19	5.2424	19	16.93	0.75	1520	-7.2799 1336 0171 3369 9630 7659
E-Hy-Cl	This work	0	19	3.30	19	37.50	0.75	1520	-7.2799 1336 0182 4599 1732 3494
Hy-Cl	This work	1	19	5.2424	19	16.93		1520	-7.2799 1316 4908 1617 1579 6632
Hy-Cl	SH (2002) [28]	1	19	4.575	19	60.75		1520	-7.2799 1316 3232 2859 8804 0630
E-Hy-Cl	This work	1	19	5.2424	19	16.93	0.75	3040	-7.2799 1341 2669 2669 4750 6538
E-Hy-Cl	This work	1	19	4.575	19	60.75	0.75	3040	-7.2799 1341 2669 2617 5311 7615
Hy-Cl	This work	2	19	5.2424	19	16.93		2280	-7.2799 1341 2454 9261 6255 1259
Hy-Cl	SH (2002) [28]	2	19	5.25	19	60.75		2280	-7.2799 1341 2448 4952 1816 7709
E-Hy-Cl	This work	2	19	5.2424	19	16.93	0.75	4560	-7.2799 1341 2669 3059 3661 7108
E-Hy-Cl	This work	2	19	5.25	19	60.75	0.75	4560	-7.2799 1341 2669 3059 6441 0982
Hy-Cl	This work	3	18	5.2424	18	16.93		2964	-7.2799 1341 2669 1097 8147 1476
Hy-Cl	SH (2002) [28]	3	18	5.85	18	60.75		2964	-7.2799 1341 2669 0963 6600 9577
E-Hy-Cl	This work	3	18	5.2424	18	16.93	0.75	5928	-7.2799 1341 2669 3059 4858 9629
E-Hy-Cl	This work	3	18	5.85	18	60.75	0.75	5928	-7.2799 1341 2669 3059 6491 4628
Hy-Cl	This work	4	15	5.2424	15	16.93		3444	-7.2799 1341 2669 3056 3412 5515
Hy-Cl	SH (2002) [28]	4	15	6.75	15	60.75		3444	-7.2799 1341 2669 3057 5506 0295
E-Hy-Cl	This work	4	15	5.2424	15	16.93	0.75	6888	-7.2799 1341 2669 3059 5063 2462
E-Hy-Cl	This work	4	15	6.75	15	60.75	0.75	6888	-7.2799 1341 2669 3059 6491 5947
Hy-Cl	This work	5	14	5.2424	14	16.93		3864	-7.2799 1341 2669 3058 1870 8148
Hy-Cl	SH (2002) [28]	5	14	7.80	14	60.75		3864	-7.2799 1341 2669 3059 6464 5118
E-Hy-Cl	This work	5	14	5.2424	14	16.93	0.75	7728	-7.2799 1341 2669 3059 5226 1075
E-Hy-Cl	This work	5	14	7.80	14	60.75	0.75	7728	-7.2799 1341 2669 3059 6491 6410
Hy-Cl	This work	6	14	5.2424	14	16.93		4284	-7.2799 1341 2669 3058 2142 9810
Hy-Cl	SH (2002) [28]	6	14	9.00	14	60.75		4284	-7.2799 1341 2669 3059 6489 6870
E-Hy-Cl	This work	6	14	5.2424	14	16.93	0.67	8568	-7.2799 1341 2669 3059 5238 6189
E-Hy-Cl	This work	6	14	5.2424	14	16.93	0.75	8568	-7.2799 1341 2669 3059 5308 4206
E-Hy-Cl	This work	6	14	9.00	14	60.75	0.67	8568	-7.2799 1341 2669 3059 6491 6611
E-Hy-Cl	This work	6	14	9.00	14	60.75	0.75	8568	-7.2799 1341 2669 3059 6491 6759
Reference ^a									-7.2799 1341 2669 3059 6491 9459

Note: All energies are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^aNakatsuji and Nakashima [38].

4.4 | E-Hy-Cl using a “doubled” basis set of exponential r_{12} factors

Channeling Hirschfelder's suggestion [17] that an exponentially correlated r_{12} paired with a linear r_{12} factor has the right kind of behavior both in the vicinity of the r_{12} cusp as r_{12} goes to 0 and as r_{12} goes to infinity, in paper I of this series we considered a simple 4 term exponentially correlated Hy (E-Hy) (which included both exponential and linear r_{12} terms) whose spacial part is

$$\Psi_{\text{E-Hy}} = e^{-\omega_{12}r_{12}} (1 + c_1 r_{12} + c_2 e^{-\omega_{12}r_{12}} + c_3 r_{12} e^{-\omega_{12}r_{12}}). \quad (17)$$

In that calculation, and indeed in all of our E-Hy-Cl calculations, we considered only a single $\omega_{12}r_{12}$ exponent (either 0.75 or 0.67 in Table 2). In Table 3 the second through fifth entries correspond to varying ω_{12} in calculations in which there is just a single ω_{12} , which is the case for all of the calculations in Table 2. From the second, third, and fifth entries in Table 3 an optimum ω_{12} value of 0.67 is obtained, which improves on the energy only in the 17th decimal digit, indicating that the energy curve is flat with respect to a single ω_{12} and there is no need to repeat the Table 2 calculations. This conclusion is verified in Table 2 where the 8568 calculations have been repeated with $\omega_{12} = 0.67$.

TABLE 3 E-Hy-Cl using a “doubled” basis set of exponential factors

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	ω'_{12}	N	Energy (hartree)
E-Hy-Cl	This work	1	13 ^a	5.2424	13	16.93	0.75	0.75	1456	-7.2799 1341 2666 7550 9600 0469
E-Hy-Cl	This work	3	13 ^b	5.2424	13	16.93	0.75	0.75	2912	-7.2799 1341 2669 3058 1179 4209
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.72	0.72	2912	-7.2799 1341 2669 3058 1332 8053
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.67	0.67	2912	-7.2799 1341 2669 3058 1783 5666
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.622	0.622	2912	-7.2799 1341 2669 3058 1383 4101
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.67	0.67	2912	-7.2799 1341 2669 3058 1783 5666
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.67	0.65	2912	-7.2799 1341 2669 3058 2045 8391
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.67	0.60	2912	-7.2799 1341 2669 3058 2345 7064
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.67	0.55	2912	-7.2799 1341 2669 3058 2118 7524
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.90	0.60	2912	-7.2799 1341 2669 3058 2409 5021
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.80	0.60	2912	-7.2799 1341 2669 3058 2542 0631
E-Hy-Cl	This work	3	13	5.2424	13	16.93	0.75	0.60	2912	-7.2799 1341 2669 3058 2063 1500
Reference ^c										-7.2799 1341 2669 3059 6491 9459

Note: All energies are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^a13 here represents $n_{\text{orbs}} = 13, 13$ respectively for $l = 0-1$.

^b13 here and below represents $n_{\text{orbs}} = 13, 13, 13$, and 13, respectively for $l = 0-3$.

^cNakatsuji and Nakashima [38].

It has been suggested that it might be reasonable to take two *different* non-linear parameters $\omega_{12}, \omega'_{12}$ corresponding to whether the exponential correlation term is paired with a linear r_{12} factor or not. Table 3 explores this. From the seventh, eighth and ninth line data points for varying ω'_{12} with $\omega_{12} = 0.67$, an optimum value of $\omega'_{12} = 0.60$ is obtained. This again improves the energy only in the 17th decimal digit, indicating that the energy is flat with respect to ω'_{12} . Finally only ω_{12} was varied, keeping ω'_{12} fixed; the entries are in Table 3 also. They give an optimized value of 0.80 which again improves on the energy only in the 17th decimal digit, indicating that the energy is flat with respect to ω_{12} as well. Indeed what stands out the most in Table 3 is how flat the energy is with respect to $\omega_{12}, \omega'_{12}$, where the results are identical through 16 decimal digits for all the 2912 term runs, so $\omega_{12} = 0.75$, the scaled value, is a good value for the exponential r_{12} value (and there is no need for a second ω_{12}). As mentioned in the previous paragraph, this conclusion is verified in Table 2 where the 8568 calculations have been repeated with $\omega_{12} = 0.67$. The results are actually worse than the $\omega_{12} = 0.75$ results, with the ‘doubled’ basis set results differing in the 18th decimal and the ‘doubled’ basis set for each different l -wave differing in the 22nd digit.

5 | EXCITED STATES OF Li^+

In the following sections excited 2^1S through 6^1S states of Li^+ will be discussed. Table 4 gives a summary of the best previous explicitly correlated variational calculations on these states, with the Thakkar [42] calculations being the best previous calculations.

5.1 | $\text{Li}^+ 2^1S$

The 2^1S state of Li^+ is the first comparison of the convergence of an E-Hy-Cl wave function expansion with that of the Hy-Cl wave function without exponential factors for excited S states; this will test whether both convergence acceleration and an improvement in precision for the same basis holds for excited states as well as the ground state. In Table 5 we again start out with the FR [22] 820 term [16s14p13d12f] wave function, this time with their $\xi = 2.310125$ for the 2^1S state, and extend it to 974 terms [18s15p14d13f]. Optimizing this exponent for 974 terms yielded $\xi = 2.46$ and the 1482 term wave function result with this exponent gives an indication of the limit for a single basis set $l_{\max} = 3, s, p, d, f$ Hy-Cl for this state, which is better than the best previous calculation, the ECS calculation of Thakkar [42].

Doubling the basis set by including the {inner,inner} set and optimizing ξ' yields a $\xi' = 7.77$ which takes the (FR) estimated precision from 8 decimal digits to 12 decimal digits. The effect of converting “doubled” basis set Hy-Cl wave functions into “doubled” basis set E-Hy-Cl wave functions is tested using the simple procedure of paper I: for each term in the wave function, add to the wave function a term also containing an exponentially correlated $e^{-\omega_{12}r_{12}}$ factor whose exponent ω_{12} is taken to be the ground state 0.75 value. One can see from Table 5 that the optimum value of ω_{12} is actually 0.33, but Table 5 shows the energy to be flat with respect to ω_{12} , changing only in the 14th decimal digit as ω_{12} varies from 0.33 to 0.75. As a sanity check on the use of $\omega_{12} = 0.75$ instead of 0.33, the 5928 term calculation in Table 5 with $\omega_{12} = 0.75$ is repeated

TABLE 4 Comparison of correlated wave function $\text{Li}^+ 1S$ excited state nonrelativistic energies

State of Li^+	Technique	Author	N	Energy (hartree)
2^1S	Hy	Pekeris [39]	444	-5.0408 7673 10
2^1S	ECS	Cann and Thakkar [40]	100	-5.0408 7673 13
2^1S	Hy-Cl	Frolov and Ruiz [22]	820	-5.0408 7674 38
2^1S	Hy	Accad et al. [41]	1078	-5.0408 7674 4
2^1S	ECS	Thakkar [42]	200	-5.0408 7674 52
3^1S	Hy	Accad et al. [41]	364	-4.7337 5225 07
3^1S	Hy-Cl	Frolov and Ruiz [22]	820	-4.7337 5581
3^1S	ECS	Cann and Thakkar [40]	100	-4.7337 5607 78
3^1S	ECS	Thakkar [42]	200	-4.7337 5613 12
4^1S	Hy	Accad et al. [41]	364	-4.6297 7505
4^1S	Hy	Perkins [43]	40	-4.6297 78
4^1S	Hy-Cl	Frolov and Ruiz [22]	820	-4.6297 8349
4^1S	ECS	Cann and Thakkar [40]	100	-4.6297 8359 73
4^1S	ECS	Thakkar [42]	200	-4.6297 8363 43
5^1S	Hy	Accad et al. [41]	364	-4.5824 1415
5^1S	Hy-Cl	Frolov and Ruiz [22]	820	-4.5824 2193
5^1S	Hy	Perkins [43]	40	-4.5824 24
5^1S	ECS	Cann and Thakkar [40]	100	-4.5824 2795 27
5^1S	ECS	Thakkar [42]	200	-4.5824 2799 10
6^1S	Hy-Cl	Frolov and Ruiz [22]	820	-4.5568 7765
6^1S	Hy	Perkins [43]	46	-4.5569 51
6^1S	ECS	Cann and Thakkar [40]	100	-4.5569 5317 70
6^1S	ECS	Thakkar [42]	200	-4.5569 5321 86

Abbreviation: ECS, Exponentially Correlated Slaters.

Note: N is the number of terms in the expansion. All energies are variational.

with $\omega_{12} = 0.33$, and they agree through 15 decimal digits with the 0.75 term result actually giving the lower energy. The ξ , ξ' , and ω_{12} values decrease by about the same factor of 2.2 in going from the ground to first excited state, representative of an electron distribution on average further away from the nucleus in an excited state.

The results are tabulated in Table 5. Since the 8568 term result is better than the best previous calculation, the formula of Pekeris and co-workers [44]:

$$E_{\text{extrapolated}} = E_1 + \frac{(E_1 - E_0)(E_2 - E_1)}{2E_1 - E_0 - E_2} \quad (18)$$

where the E_0 , E_1 and E_2 values are the 6888, 7728 and 8568 term results in Table 5), is used to extrapolate to an estimated exact non-relativistic energy of this state.

These Table 5 results show dramatic improvements:

1. Hy-Cl s -wave 4 decimal place precision becomes 7 decimal place E-Hy-Cl s -wave precision ($>$ Hy-Cl p -wave precision),
2. Hy-Cl p -wave 6 decimal place precision becomes 14 decimal place E-Hy-Cl p -wave precision ($>$ Hy-Cl $l = 6$ precision),
3. Hy-Cl d -wave 10 decimal place precision becomes 14 decimal place E-Hy-Cl d -wave precision ($>$ Hy-Cl $l = 6$ precision),
4. From here on, convergence gets slower, but already at the E-Hy-Cl p -wave expansion, the result is better than the Hy-Cl $l = 6$ result.

It is clear from the Table 5 results that the 14 decimal place $l = 6$ Hy-Cl result can be improved on with just an $l = 2$ E-Hy-Cl basis. Note that a 16 decimal digit precision E-Hy-Cl result has been obtained with just two ξ, ξ' exponents.

TABLE 5 Comparison of theoretical E-Hy-Cl and Hy-Cl energies for the 2^1S Li^+ excited state using a “doubled” basis set of orbitals

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-Cl	FR (2010) [22]	3	16 ^a	2.3101 25				820	−5.0408 7674 38
Hy-Cl	This work	3	18 ^b	2.46				974	−5.0408 7674 5044 9696 1881
Hy-Cl	This work	3	19 ^c	2.46				1482	−5.0408 7674 5370 5547 1125
E-Hy-Cl	This work	3	13 ^d	2.46	13	7.77	0.75	2912	−5.0408 7674 5595 4128 6324
E-Hy-Cl	This work	3	13	2.46	13	7.77	0.50	2912	−5.0408 7674 5595 4287 4604
E-Hy-Cl	This work	3	13	2.46	13	7.77	0.35	2912	−5.0408 7674 5595 4300 3608
E-Hy-Cl	This work	3	13	2.46	13	7.77	0.33	2912	−5.0408 7674 5595 4302 5725
E-Hy-Cl	This work	3	13	2.46	13	7.77	0.30	2912	−5.0408 7674 5595 4300 2471
Hy-Cl	This work	0	19	2.46	19	7.77		760	−5.0408 2460 4907 4930 4496
E-Hy-Cl	This work	0	19	2.46	19	7.77	0.75	1520	−5.0408 7673 7965 6733 1416
Hy-Cl	This work	1	19	2.46	19	7.77		1520	−5.0408 7669 8261 6176 4450
E-Hy-Cl	This work	1	19	2.46	19	7.77	0.75	3040	−5.0408 7674 5595 4320 3693
Hy-Cl	This work	2	19	2.46	19	7.77		2280	−5.0408 7674 5538 3484 4326
E-Hy-Cl	This work	2	19	2.46	19	7.77	0.75	4560	−5.0408 7674 5595 4383 7884
Hy-Cl	This work	3	18	2.46	18	7.77		2964	−5.0408 7674 5595 3575 7861
E-Hy-Cl	This work	3	18	2.46	18	7.77	0.33	5928	−5.0408 7674 5595 4386 5314
E-Hy-Cl	This work	3	18	2.46	18	7.77	0.75	5928	−5.0408 7674 5595 4389 6091
Hy-Cl	This work	4	15	2.46	15	7.77		3444	−5.0408 7674 5595 4297 3975
E-Hy-Cl	This work	4	15	2.46	15	7.77	0.75	6888	−5.0408 7674 5595 4391 8347
Hy-Cl	This work	5	14	2.46	14	7.77		3864	−5.0408 7674 5595 4299 9740
E-Hy-Cl	This work	5	14	2.46	14	7.77	0.75	7728	−5.0408 7674 5595 4392 7648
Hy-Cl	This work	6	14	2.46	14	7.77		4284	−5.0408 7674 5595 4301 8911
E-Hy-Cl	This work	6	14	2.46	14	7.77	0.75	8568	−5.0408 7674 5595 4393 3350
Extrapolated	This work			2.46		7.77	0.75		−5.0408 7674 5595 4394(1)
Reference ^e									−5.0408 7674 52

Note: All energies (except extrapolated) are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^a16 here and below represents $n_{\text{orbs}} = 16, 14, 13,$ and $12,$ respectively for $l = 0-3.$

^b18 here and below represents $n_{\text{orbs}} = 18, 15, 14,$ and $13,$ respectively for $l = 0-3.$

^c19 here represents $n_{\text{orbs}} = 19, 19, 19,$ and $18,$ respectively for $l = 0-3.$

^d13 here represents $n_{\text{orbs}} = 13, 13, 13,$ and $13,$ respectively for $l = 0-3.$

^eThakkar [42].

5.2 | $Li^+ 3^1S$

The 2^1S state of Li^+ demonstrated that both convergence acceleration and an improvement in precision for the same basis without exponential factors holds for the first excited S state. Here we consider the second excited state of S symmetry, the 3^1S state of $Li^+.$ In moving on to higher and higher excited states of S symmetry, the electron distribution on average is further and further away from the nucleus and more diffuse, so it is worth examining what effect if any adding an exponential r_{12} factor has. Table 6 again starts out with the FR [22] 820 term [16s14p13d12f] wave function, this time with their $\xi = 1.703409$ for the 3^1S state, and extends it to 974 terms [18s15p14d13f]. Optimizing this exponent for 974 terms yielded $\xi = 1.55$ and the 1482 term wave function result with this exponent gives an indication of the limit for a single basis set $l_{\max} = 3, s, p, d, f$ Hy-Cl for this state.

Doubling the basis set and optimizing ξ' takes the (FR) estimated precision from 6 decimal digits to 12 decimal digits. The ξ and ξ' values decrease by about the same factor of 1.59 in going from the first to the second excited 1S state, again representative of an electron distribution further away from the nucleus in an excited state. Optimizing ω_{12} yields an ω_{12} that decreases by even more than 1.59, for which we have no explanation. The results for converting ‘doubled’ basis set Hy-Cl wave functions into ‘doubled’ basis set E-Hy-Cl wave functions are tabulated in Table 6 along with an extrapolated result obtained using Equation (18). These results show:

1. Hy-Cl s-wave 4 decimal place precision becomes 7 decimal place E-Hy-Cl s-wave precision ($>$ Hy-Cl p-wave precision),

TABLE 6 Comparison of theoretical E-Hy-Cl and Hy-Cl energies for the 3^1S Li^+ excited state using a “doubled” basis set of orbitals

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-Cl	FR (2010) [22]	3	16 ^a	1.7034 09				820	−4.7337 5581
Hy-Cl	This work	3	18 ^b	1.55				974	−4.7337 5612 9039 6601 1607
Hy-Cl	This work	3	19 ^c	1.55				1482	−4.7337 5613 0146 6871 3462
Hy-Cl	This work	0	19	1.55	19	4.89		760	−4.7337 4189 7343 8298 2686
E-Hy-Cl	This work	0	19	1.55	19	4.89	0.1165	1520	−4.7337 5612 4622 9742 7653
Hy-Cl	This work	1	19	1.55	19	4.89		1520	−4.7337 5612 1061 5465 0694
E-Hy-Cl	This work	1	19	1.55	19	4.89	0.1165	3040	−4.7337 5613 2647 7113 3880
Hy-Cl	This work	2	19	1.55	19	4.89		2280	−4.7337 5613 2635 4770 5599
E-Hy-Cl	This work	2	19	1.55	19	4.89	0.1165	4560	−4.7337 5613 2647 7432 3919
Hy-Cl	This work	3	18	1.55	18	4.89		2964	−4.7337 5613 2647 6273 6497
E-Hy-Cl	This work	3	18	1.55	18	4.89	0.1165	5928	−4.7337 5613 2647 7493 9610
Hy-Cl	This work	4	15	1.55	15	4.89		3444	−4.7337 5613 2647 6438 7317
E-Hy-Cl	This work	4	15	1.55	15	4.89	0.1165	6888	−4.7337 5613 2647 7533 6627
Hy-Cl	This work	5	14	1.55	14	4.89		3864	−4.7337 5613 2647 6456 6611
E-Hy-Cl	This work	5	14	1.55	14	4.89	0.1165	7728	−4.7337 5613 2647 7545 8921
Hy-Cl	This work	6	14	1.55	14	4.89		4284	−4.7337 5613 2647 6476 7372
E-Hy-Cl	This work	6	14	1.55	14	4.89	0.1165	8568	−4.7337 5613 2647 7554 9793
Extrapolated	This work			1.55		4.89	0.1165		−4.7337 5613 2647 758(3)
Reference ^d									−4.7337 5613 12

Note: All energies (except extrapolated) are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^a16 here represents $n_{\text{orbs}} = 16, 14, 13,$ and $12,$ respectively for $l = 0-3.$

^b18 here and below represents $n_{\text{orbs}} = 18, 15, 14,$ and $13,$ respectively for $l = 0-3.$

^c19 here represents $n_{\text{orbs}} = 19, 19, 19,$ and $18,$ respectively for $l = 0-3.$

^dThakkar [42].

- Hy-Cl p -wave 7 decimal place precision becomes 13 decimal place E-Hy-Cl p -wave precision ($>$ Hy-Cl $l = 5$ precision),
- Hy-Cl d -wave 10 decimal place precision becomes 13 decimal place E-Hy-Cl d -wave precision ($>$ Hy-Cl $l = 6$ precision),
- From here on, convergence gets slower, but already at the E-Hy-Cl p -wave expansion, the result is better than the Hy-Cl $l = 5$ result.

These results show that the 14 decimal place $l = 6$ Hy-Cl result can be improved on with just an $l = 2$ E-Hy-Cl basis. Note that a 15 decimal digit precision E-Hy-Cl result (almost as good as the 16 decimal digit 2^1S) has been obtained with just two ξ, ξ' exponents.

5.3 | $Li^+ 4^1S$

Table 7 gives the results for optimizing ξ, ξ' and ω_{12} to 1.0586, 2.103 and 0.125, respectively, as well as the 1482 term result which is intended to give an indication of the limit for a single basis set $l_{\max} = 3, s, p, d, f$ Hy-Cl for this state. Table 7 also explores the effect of converting ‘doubled’ basis set Hy-Cl wave functions into ‘doubled’ basis set E-Hy-Cl wave functions and includes an extrapolated result obtained using Equation (18). These results show:

- Hy-Cl s -wave 4 decimal place precision becomes 8 decimal place E-Hy-Cl s -wave precision ($>$ Hy-Cl p -wave precision),
- Hy-Cl p -wave 8 decimal place precision becomes 11 decimal place E-Hy-Cl p -wave precision ($>$ Hy-Cl $l = 6$ precision),
- Hy-Cl d -wave 10 decimal place precision becomes 11 decimal place E-Hy-Cl d -wave precision ($>$ Hy-Cl $l = 6$ precision),
- From here on, Hy-Cl convergence gets slower, but already at the E-Hy-Cl p -wave expansion, the result is almost as good as the Hy-Cl $l = 6$ result, and the E-Hy-Cl result continues to become more precise.

These results show that the 10 decimal place $l = 6$ Hy-Cl result can be improved on with just an $l = 1$ E-Hy-Cl basis. Note that a result of 16 decimal digit precision has been obtained with just two ξ, ξ' exponents.

TABLE 7 Comparison of theoretical E-Hy-Cl and Hy-Cl energies for the 4^1S Li^+ excited state using a “doubled” basis set of orbitals

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-Cl	FR (2010) [22]	3	16 ^a	0.9784 34				820	−4.6297 8349
Hy-Cl	This work	3	18 ^b	1.0586				974	−4.6297 8360 9059 5590 0765
Hy-Cl	This work	3	19 ^c	1.0586				1482	−4.6297 8362 6796 8672 5058
Hy-Cl	This work	0	19	1.0586	19	2.103		760	−4.6297 7781 3269 1200 8701
E-Hy-Cl	This work	0	19	1.0586	19	2.103	0.125	1520	−4.6297 8363 4616 1219 3287
Hy-Cl	This work	1	19	1.0586	19	2.103		1520	−4.6297 8363 3125 2370 6566
E-Hy-Cl	This work	1	19	1.0586	19	2.103	0.125	3040	−4.6297 8363 7871 7957 5015
Hy-Cl	This work	2	19	1.0586	19	2.103		2280	−4.6297 8363 7857 0586 6931
E-Hy-Cl	This work	2	19	1.0586	19	2.103	0.125	4560	−4.6297 8363 7874 9632 4191
Hy-Cl	This work	3	18	1.0586	18	2.103		2964	−4.6297 8363 7864 1691 2919
E-Hy-Cl	This work	3	18	1.0586	18	2.103	0.125	5928	−4.6297 8363 7876 3953 0948
Hy-Cl	This work	4	15	1.0586	15	2.103		3444	−4.6297 8363 7864 5988 6374
E-Hy-Cl	This work	4	15	1.0586	15	2.103	0.125	6888	−4.6297 8363 7876 7620 1923
Hy-Cl	This work	5	14	1.0586	14	2.103		3864	−4.6297 8363 7865 1846 1588
E-Hy-Cl	This work	5	14	1.0586	14	2.103	0.125	7728	−4.6297 8363 7876 9655 0767
Hy-Cl	This work	6	14	1.0586	14	2.103		4284	−4.6297 8383 7865 5159 9007
E-Hy-Cl	This work	6	14	1.0586	14	2.103	0.125	8568	−4.6297 8363 7876 9730 9637
Extrapolated	This work			1.0586		2.103	0.125		−4.6297 8363 7876 9734(3)
Reference ^d									−4.6297 8363 43

Note: All energies (except extrapolated) are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^a16 here represents $n_{\text{orbs}} = 16, 14, 13,$ and $12,$ respectively for $l = 0-3.$

^b18 here and below represents $n_{\text{orbs}} = 18, 15, 14,$ and $13,$ respectively for $l = 0-3.$

^c19 here represents $n_{\text{orbs}} = 19, 19, 19,$ and $18,$ respectively for $l = 0-3.$

^dThakkar [42].

5.4 | $Li^+ 5^1S$

Table 8 gives the results for optimizing ξ, ξ' and ω_{12} to 0.832, 1.35 and 0.039, respectively, as well as the 1482 term result which is intended to give an indication of the limit for a single basis set $l_{\max} = 3, s, p, d, f$ Hy-Cl for this state. Table 8 also explores the effect of converting ‘doubled’ basis set Hy-Cl wave functions into ‘doubled’ basis set E-Hy-Cl wave functions and includes an extrapolated result obtained using Equation (18). In the table both the optimized value for $\omega_{12}, 0.039,$ and the 4^1S value of 0.125 are included for $l = 0, 1$ and 2 ($N = 1520, 3040,$ and 4560) and in each case the 4^1S value of 0.125 gives a better energy, so $\omega_{12} = 0.125$ is chosen for 5 and higher 1S states. These results show:

1. Hy-Cl s -wave 5 decimal place precision becomes 8 decimal place E-Hy-Cl s -wave precision ($>$ Hy-Cl p -wave precision),
2. Hy-Cl p -wave 8 decimal place precision becomes 10 decimal place E-Hy-Cl p -wave precision ($>$ Hy-Cl $l = 6$ precision),
3. From here on, convergence gets slower, but already at the E-Hy-Cl d -wave expansion, the result is almost as good as the Hy-Cl $l = 6$ result.

These results show that the $l = 6$ Hy-Cl result can be improved on with just an $l = 1$ E-Hy-Cl basis. Note that a result of 11 decimal digit precision can be obtained with two ξ, ξ' exponents.

5.5 | $Li^+ 6^1S$

Table 9 starts out with the FR [22] 820 term $[16s14p13d12f]$ wave function with $\xi = 0.6917 01$ and the 974 term $[18s15p14d13f]$ wave function with 974 term optimized exponent $\xi = 0.729.$ Then follows the 1482 term wave function result with this exponent which gives an indication of the limit for a single basis set $l_{\max} = 3, s, p, d, f$ Hy-Cl for this state. The rest of the table explores the effect of converting “doubled” basis set Hy-Cl wave functions into “doubled” basis set E-Hy-Cl wave functions and includes an extrapolated result obtained using Equation (18). These results show:

TABLE 8 Comparison of theoretical E-Hy-Cl and Hy-Cl energies for the 5^1S Li^+ excited state using a “doubled” basis set of orbitals

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-Cl	FR (2010) [22]	3	16 ^a	0.8910 26				820	−4.5824 2193
Hy-Cl	This work	3	18 ^b	0.8532				974	−4.5824 2760 0574 4199 1556
Hy-Cl	This work	3	19 ^c	0.8532				1482	−4.5824 2792 3044 9567 7158
E-Hy-Cl	This work	3	13 ^d	0.8532	13	1.35	0.125	2912	−4.5824 2798 6509 4044 7702
E-Hy-Cl	This work	3	13	0.8532	13	1.35	0.039	2912	−4.5824 2798 9025 0683 2748
E-Hy-Cl	This work	3	13	0.8532	13	1.35	0.010	2912	−4.5824 2798 8844 0602 4140
Hy-Cl	This work	0	19	0.8532	19	1.35		760	−4.5824 2503 4776 5722 3871
E-Hy-Cl	This work	0	19	0.8532	19	1.35	0.039	1520	−4.5824 2799 0962 6431 2460
E-Hy-Cl	This work	0	19	0.8532	19	1.35	0.125	1520	−4.5824 2799 1492 9360 6528
Hy-Cl	This work	1	19	0.8532	19	1.35		1520	−4.5824 2799 0919 0871 7327
E-Hy-Cl	This work	1	19	0.8532	19	1.35	0.039	3040	−4.5824 2799 3780 4629 7365
E-Hy-Cl	This work	1	19	0.8532	19	1.35	0.125	3040	−4.5824 2799 3801 7657 8376
Hy-Cl	This work	2	19	0.8532	19	1.35		2280	−4.5824 2799 3584 6669 2392
E-Hy-Cl	This work	2	19	0.8532	19	1.35	0.039	4560	−4.5824 2799 3832 5468 7460
E-Hy-Cl	This work	2	19	0.8532	19	1.35	0.125	4560	−4.5824 2799 3844 9820 8253
Hy-Cl	This work	3	18	0.8532	18	1.35		2964	−4.5824 2799 3713 5868 4696
E-Hy-Cl	This work	3	18	0.8532	18	1.35	0.125	5928	−4.5824 2799 3858 3683 8602
Hy-Cl	This work	4	15	0.8532	15	1.35		3444	−4.5824 2799 3725 0432 3580
E-Hy-Cl	This work	4	15	0.8532	15	1.35	0.125	6888	−4.5824 2799 3864 6188 0634
Hy-Cl	This work	5	14	0.8532	14	1.35		3864	−4.5824 2799 3727 2825 0421
E-Hy-Cl	This work	5	14	0.8532	14	1.35	0.125	7728	−4.5824 2799 3865 1089 6521
Hy-Cl	This work	6	14	0.8532	14	1.35		4284	−4.5824 2799 3738 9437 6777
E-Hy-Cl	This work	6	14	0.8532	14	1.35	0.125	8568	−4.5824 2799 3866 1321 6656
Extrapolated	This work			0.8532		1.35			−4.5824 2799 3869(3)
Reference ^e									−4.5824 2799 10

Note: All energies (except extrapolated) are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^a16 here represents $n_{\text{orbs}} = 16, 14, 13,$ and $12,$ respectively for $l = 0-3.$

^b18 here and below represents $n_{\text{orbs}} = 18, 15, 14,$ and $13,$ respectively for $l = 0-3.$

^c19 here represents $n_{\text{orbs}} = 19, 19, 19,$ and $18,$ respectively for $l = 0-3.$

^d13 here and below represents $n_{\text{orbs}} = 13, 13, 13,$ and $13,$ respectively for $l = 0-3.$

^eThakkar [42].

1. Hy-Cl s -wave 5 decimal place precision becomes 6 decimal place E-Hy-Cl s -wave precision.
2. Hy-Cl p -wave 6 decimal place precision becomes 7 decimal place E-Hy-Cl p -wave precision ($>$ Hy-Cl h -wave precision),
3. Hy-Cl d -wave 6 decimal place precision becomes 9 decimal place E-Hy-Cl d -wave precision ($>$ Hy-Cl $l = 6$ precision),
4. From here on, convergence gets slower, but already at the E-Hy-Cl d -wave expansion, the result is better than the Hy-Cl $l = 6$ result.

These results show that the 8 decimal place $l = 6$ Hy-Cl result can be improved on with just an $l = 2$ E-Hy-Cl basis. Note that a results of 10 decimal digit precision can be obtained with just two ξ, ξ' exponents.

6 | CONCLUSION

Table 10 summarizes our results along with the best previous correlated wave function method calculations employing STOs. The renewed interest in these methods is coming from the incredible accuracy of experiments these days, which necessitates the use of correlated wave functions to do as well or better theoretically. Of these methods Hy-Cl and E-Hy-Cl stand alone because their formalism with at most a single $r_{ij}^{\nu_{ij}} e^{-\omega_{ij} r_{ij}}$ factor per term ($\omega_{ij} = 0$ for Hy-Cl) leads to solvable integrals for $N > 4$ electrons and hence does not limit the methods to systems with $N \leq 4.$

TABLE 9 Comparison of theoretical E-Hy-Cl and Hy-Cl energies for the 6^1S Li^+ excited state using a “doubled” basis set of orbitals

Technique	Author	l_{\max}	n_{orbs}	ξ	n'_{orbs}	ξ'	ω_{12}	N	Energy (hartree)
Hy-Cl	FR (2010) [22]	3	16 ^a	0.6917 01				820	−4.5568 7765
Hy-Cl	This work	3	18 ^b	0.729				974	−4.5569 4089 3519 2714 5155
Hy-Cl	This work	3	19 ^c	0.729				1482	−4.5569 5179 6694 9568 1369
Hy-Cl	This work	0	19	0.729	19	1.10		760	−4.5569 5109 4698 7315 5977
E-Hy-Cl	This work	0	19	0.729	19	1.10	0.125	1520	−4.5569 5311 5172 0210 9381
Hy-Cl	This work	1	19	0.729	19	1.10		1520	−4.5569 5316 2963 8092 8612
E-Hy-Cl	This work	1	19	0.729	19	1.10	0.125	3040	−4.5569 5321 9255 6118 4070
Hy-Cl	This work	2	19	0.729	19	1.10		2280	−4.5569 5318 8286 0171 5336
E-Hy-Cl	This work	2	19	0.729	19	1.10	0.125	4560	−4.5569 5322 3557 4262 9478
Hy-Cl	This work	3	18	0.729	18	1.10		2964	−4.5569 5321 5600 5527 5954
E-Hy-Cl	This work	3	18	0.729	18	1.10	0.125	5928	−4.5569 5322 3803 0398 5848
Hy-Cl	This work	4	15	0.729	15	1.10		3444	−4.5569 5321 7738 1366 5240
E-Hy-Cl	This work	4	15	0.729	15	1.10	0.125	6888	−4.5569 5322 3847 1581 0275
Hy-Cl	This work	5	14	0.729	14	1.10		3864	−4.5569 5321 9105 3404 9757
E-Hy-Cl	This work	5	14	0.729	14	1.10	0.125	7728	−4.5569 5322 3860 6173 3418
Hy-Cl	This work	6	14	0.729	14	1.10		4284	−4.5569 5322 0363 5865 1121
E-Hy-Cl	This work	6	14	0.729	14	1.10	0.125	8568	−4.5569 5322 3871 2813 8893
Extrapolated	This work			0.729		1.10	0.125		−4.5569 5322 391(4)
Reference ^d									−4.5569 5321 86

Note: All energies (except Extrapolated) are variational; all calculations were done in quadruple-double-with exponent (QDE) precision.

^a16 here represents $n_{\text{orbs}} = 16, 14, 13,$ and $12,$ respectively for $l = 0-3.$

^b18 here represents $n_{\text{orbs}} = 18, 15, 14,$ and $13,$ respectively for $l = 0-3.$

^c19 here represents $n_{\text{orbs}} = 19, 19, 19,$ and $18,$ respectively for $l = 0-3.$

^dThakkar [42].

TABLE 10 Comparison of correlated wave function $Li^+ 1S$ excited state nonrelativistic energies

State of Li^+	Technique	Author	N	Energy (hartree)
2^1S	Hy	Accad et al. [41]	1078	−5.0408 7674 4
2^1S	Hy-Cl	Frolov and Ruiz [22]	820	−5.0408 7674 38
2^1S	ECS	Thakkar [42]	200	−5.0408 7674 52
2^1S	E-Hy-Cl	This work	8568	−5.0408 7674 5595 4393
2^1S	Extrapolated	This work		−5.0408 7674 5595 4394(1)
3^1S	Hy	Accad et al. [41]	364	−4.7337 5225 07
3^1S	Hy-Cl	Frolov and Ruiz [22]	820	−4.7337 5581
3^1S	ECS	Thakkar [42]	200	−4.7337 5613 12
3^1S	E-Hy-Cl	This work	8568	−4.7337 5613 2647 7555
3^1S	Extrapolated	This work		−4.7337 5613 2647 758(3)
4^1S	Hy	Perkins [43]	40	−4.6297 78
4^1S	Hy-Cl	Frolov and Ruiz [22]	820	−4.6297 8349
4^1S	ECS	Thakkar [42]	200	−4.6297 8363 43
4^1S	E-Hy-Cl	This work	8568	−4.6297 8363 7876 9731
4^1S	Extrapolated	This work		−4.6297 8363 7876 9734(3)
5^1S	Hy-Cl	Frolov and Ruiz [22]	820	−4.5824 2193
5^1S	Hy	Perkins [43]	40	−4.5824 24
5^1S	ECS	Thakkar [42]	200	−4.5824 2799 10
5^1S	E-Hy-Cl	This work	8568	−4.5824 2799 3866 1322

(Continues)

TABLE 10 (Continued)

State of Li^+	Technique	Author	N	Energy (hartree)
$5\ ^1S$	Extrapolated	This work		-4.5824 2799 3869(3)
$6\ ^1S$	Hy-Cl	Frolov and Ruiz [22]	820	-4.5568 7765
$6\ ^1S$	Hy	Perkins [43]	46	-4.5569 51
$6\ ^1S$	ECS	Thakkar [42]	200	-4.5569 5321 86
$6\ ^1S$	E-Hy-Cl	This work	8568	-4.5569 5322 3871 2814
$6\ ^1S$	Extrapolated	This work		-4.5569 5322 391(4)

Abbreviation: ECS, Exponentially Correlated Slaters.

Note: N is the number of terms in the expansion. All energies (except extrapolated) are variational.

Paper I of this series demonstrated that Hy-Cl and E-Hy-Cl are capable of greater than 20 digit accuracy for the ground state of helium, and Hy-Cl has been utilized to produce high precision results for not only ground states but excited states as well for two-, three-, and four-electron atoms and ions. Convergence acceleration was also demonstrated in paper I for the ground state of helium by comparing the convergence of the E-Hy-Cl wave function expansion to that of the Hy-Cl wave function without exponential factors. In this paper the same analysis has been extended to excited states of 1S symmetry by examining excited states of the Li^+ ion, and it has been shown that an $l = 6$ Hy-Cl result can be improved on with just an $l = 2$ E-Hy-Cl basis for most states, ($l = 3$ for the ground state in the worst case and $l = 1$ for the $6\ ^1S$ state). Ultimately the E-Hy-Cl convergence resembles that of Hy-Cl, but as pointed out in paper I it is the very dramatic convergence improvements of s -, p -, d - and f -wave E-Hy-Cl expansions compared to the Hy-Cl l -wave expansions that is important, because it offers a way of overcoming the ultimately slow convergence of “the $r_{12}r_{34}$ ” double cusp, analogous to the r_{12} cusp problem for Cl, that arises for $N \geq 4$ electron systems. This makes the application of the E-Hy-Cl method to systems with $N > 4$ worthy of investigation.

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AUTHOR CONTRIBUTIONS

James S. Sims: Conceptualization; formal analysis; investigation; methodology; resources; software; supervision; validation; writing – original draft; writing – review and editing. **Bholanath Padhy:** Conceptualization; formal analysis; methodology; writing – review and editing. **María Belén Ruiz:** Conceptualization; formal analysis; investigation; methodology; validation; writing – review and editing.

ENDNOTES

- ¹ In paper I of this series [7] this was attributed to Handy [8]. We thank an anonymous referee for pointing out that Bunge had pointed this out 3 years earlier than Handy.
- ² For our previous study, paper I in this series, see Sims et al. [7].
- ³ In their paper Wang et al. [16] refer to this as extended Hy-Cl. The authors of this paper prefer exponentially correlated Hy-Cl since there is more than one way Hy-Cl could be extended and exponentially correlated makes clear that the extension is an exponential r_{ij} factor.
- ⁴ For a review of both Hy-Cl and E-Hy-Cl, see Ruiz et al. [23].
- ⁵ There is a misprint in section 3 of our recent study. Equation 18 there should be the same as Equation 16 above, but is missing the L,M projection operator.
- ⁶ For a good review, see Drake [36], where Drake says that “doubling” the basis set leads to a dramatic improvement in precision and points out that they are closely related to the “double zeta” basis sets widely used since some of the earliest Cl calculations [37].
- ⁷ The basis set notation here is the same as in the tables, that is, $16s$ means 16 s orbitals, $14p$ means 14 p orbitals, and so forth. Since our STOs run from $n = l + 1$ to $l + n_{\text{orbs}}$, [16s14p13d12f] could also be written as 1:16s 2:15p 3:15d 4:15f.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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