

Binding Energy of ${}^7\text{Li}_2$ Molecules in Free Space and in Vapor

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Abstract

The problem of two ${}^7\text{Li}$ atoms interacting in free space via the Hulburt-Hirschfelder (HH) potential is solved in the discrete (bound-state) region. This is accomplished by solving the Lippmann-Schwinger t-matrix equation for negative-definite eigenenergies. The method used is a highly efficient matrix-inversion technique. The results are also valid for ${}^7\text{Li}$ vapor in the zero-density limit. The agreement with experiment is good. The problem is then generalized to the (low-dense) vapor by introducing an effective atomic mass and an effective binary interaction. The limitations of the present calculations are underlined.

Keywords: Bound-state region, Binding energy, Lithium-7 (${}^7\text{Li}$), Hulburt-Hirshfelder (HH) potential.

1. Introduction

The aim of this work is twofold: first, to determine the binding energy of two ${}^7\text{Li}$ atoms in free space; or, equivalently, in the zero-density ${}^7\text{Li}$ vapor; and, second, to determine this energy in the (low-dense) vapor. The methods used hinge on solving the Lippmann-Schwinger t-matrix equation after some simplifying manipulations. The resulting integral equations are of the Fredholm type (Mathews and Walker, 1969), and are solved using a well-tested matrix-inversion method (Ghassib *et al.*, 1976; Bishop *et al.*, 1977).

Just as in any other scattering, or many-body, problem, the main input here is the interatomic potential $V(r)$, r being the interatomic separation. This is central and static; it

is taken in the present work as the Hulburt-Hirschfelder (HH) potential (Holland and Biolsi, 1987).

${}^7\text{Li}$ is a chemical element with atomic number $Z = 3$. It is a highly reactive alkali metal. Its melting point is 453.65 K (Lide, 2005), and its boiling point is 1603 K. The vapor undergoes Bose-Einstein condensation (BEC) at very low temperatures, $T \sim 100\text{-}400$ nK (Bradley *et al.*, 1995).

The vibrational thermodynamic properties (the mean energy, specific heat capacity, free energy, and entropy) were calculated for the Li_2 dimer, the contribution of vibrations to the molecular partition function and to the stability of BEC being carefully examined (Jia *et al.*, 2017). The thermodynamic properties of Li vapor were studied in the temperature-range 700-2000 K, using analytic two-body potential functions for the ground singlet, and the excited triplet, molecular states (Castro *et al.*, 1990). Both scattering and S-wave bound-state properties were determined along similar lines to those of the present study for three inert gases: ${}^{20}\text{Ne}$, ${}^{40}\text{Ar}$, and ${}^{84}\text{Kr}$ (Darabee, 2017). The same theoretical framework was applied to ${}^{133}\text{Cs}$ (Alkurdi *et al.*, 2019). Another type of calculation for the thermodynamic properties of ${}^{87}\text{Rb}$ was undertaken, starting with a computation of the quantum second virial coefficient (Al Ajaleen *et al.*, 2019). The energies, equilibrium geometries, and harmonic frequencies of the triplet excited state were determined by invoking the so-called *cluster-configuration interaction method* (Heng *et al.*, 2005).

This paper is organized as follows. The formalism is presented in Section 2. The results follow in Section 3. Finally, the paper closes with some general remarks (Section 4).

2. Formalism

2.1 Interatomic potential

As already mentioned, $V(r)$ has been chosen in this work to be the HH potential which reads (Holland and Biolsi, 1987)

$$V(r) = D_e \left[\begin{aligned} & \exp\left(-2a\left(\frac{r}{r_e} - 1\right)\right) - 2 \exp\left(-a\left(\frac{r}{r_e} - 1\right)\right) + \beta\left(\frac{r}{r_e} - 1\right)^3 \\ & \times \left(1 + \gamma\left(\frac{r}{r_e} - 1\right) \exp\left(-2a\left(\frac{r}{r_e} - 1\right)\right)\right) \end{aligned} \right] \quad (1)$$

The respective parameters for both the singlet and triplet states are listed in Table 1.

Table 1: The HH parameters for the singlet (Hulburt and Hirschfelder, 1941) and triplet states, for Li-Li scattering, obtained from spectroscopic data.

Parameter	Singlet	Triplet
ω_e [cm^{-1}]	351.346	73.0
$\omega_e\chi_e$ [cm^{-1}]	2.557	3.95
β_e [cm^{-1}]	0.67293	0.329
α_e [cm^{-1}]	0.00719	0.0302
r_e [\AA]	2.6723	4.169
E [eV]	1.16284	0.041
a	2.21127	3.48507
a_0	45861	4049.39
a_1	-1.92976	-4.39459
a_2	2.1218	16.1364
β	1.3765	-11.0467
γ	1.8274	-2.9818
c	0.1272	-0.2610
b	0.825	-0.856

2.2 In free space

For two interacting ${}^7\text{Li}$ atoms in free space (or, alternatively, within the vapor in the zero-density limit), the Schrödinger equation is

$$\left[-\left(\frac{\hbar^2}{m}\right)\nabla^2 + V(\mathbf{r}) \right] \psi_{ij}^\ell(\mathbf{r}) = E \psi_{ij}^\ell(\mathbf{r}), \quad (2)$$

where $\psi_{ij}^\ell(\mathbf{r})$ is the two-body wave function for the interacting pair with relative angular momentum ℓ , m is the ${}^7\text{Li}$ atomic mass = 7.0160034366 au, \hbar is Dirac's constant (= $h/2\pi$), and the energy eigenvalue $E \equiv -|E|$ is negative-definite in the discrete (bound-state) region. In this paper, a natural system of units is occasionally used such that $\hbar = 1 = m$; all physical quantities will then be expressible only in terms of the dimension of length, L . The conversion factor is $\hbar^2/m = 6.913405495 \text{ K}\cdot\text{\AA}^2$.

Transforming Eq. (2) onto momentum space by applying the Fourier transform of $\psi_{ij}^\ell(\mathbf{r})$:

$$\psi_{ij}^\ell(\vec{\mathbf{r}}) = (2\pi)^{-3} \int \psi_{ij}^\ell(\vec{\mathbf{p}}) e^{-i\vec{\mathbf{p}}\cdot\vec{\mathbf{r}}} d\vec{\mathbf{r}}, \quad (3)$$

$\vec{\mathbf{p}}$ being the relative linear momentum of the pair, and using partial-wave decomposition, one obtains

$$\left(p^2 + \frac{m|E|}{\hbar^2} \right) \psi_{ij}^\ell(p) = - \int_0^\infty \frac{q^2 dq}{2\pi^2} \frac{m}{\hbar^2} V_\ell(p, q) \psi_{ij}^\ell(q). \quad (4)$$

Here $V_\ell(p, q)$ is the Fourier-Bessel transform of $V(r)$:

$$V_\ell(p, q) = 4\pi \int_0^\infty dr r^2 j_\ell(pr) V(r) j_\ell(qr), \quad (5)$$

$j_\ell(x)$ being the spherical Bessel function of order ℓ and argument x .

The kernel of the integral in Eq. (5) is asymmetric. Before applying standard matrix-inversion techniques, one needs to symmetrize this kernel through the following definitions:

$$\Psi_{ij}^\ell(p) \equiv \tilde{g}_\ell(p) p^{-1} (p^2 + \varepsilon)^{-1/2}; \quad (6)$$

$$\varepsilon \equiv p^2 + \frac{m|E|}{\hbar^2}. \quad (7)$$

Then Eq. (4) becomes

$$\tilde{g}_\ell(p) = -\lambda_{ij} \int_0^\infty dq \frac{pq}{2\pi^2} \frac{2\mu_{ij}}{\hbar^2} V_\ell(p, q) [(p^2 + \varepsilon)(q^2 + \varepsilon)]^{-1/2} \tilde{g}_\ell(q). \quad (8)$$

Rearranging, one gets

$$\int_0^\infty dq \frac{pq}{2\pi^2} \frac{2\mu_{ij}}{\hbar^2} V_\ell(p, q) [(p^2 + \varepsilon)(q^2 + \varepsilon)]^{-1/2} \tilde{g}_\ell(q) = \lambda_{ij} g, \quad (9)$$

λ_{ij} being the new eigenvalue:

$$\lambda_{ij} \equiv -\frac{m}{2\mu_{ij}} = -1; \quad (10)$$

$$\mu_{ij} = \frac{m_i m_j}{m_i + m_j} \equiv \text{the reduced mass of particles } i \text{ and } j. \quad (11)$$

= 1/2 m in the present case.

The substitution $g_\ell(p) = [w(p)]^{-1/2} \tilde{g}_\ell(p)$ into Eq. (9) yields the finite-dimensional matrix eigenvalue equation $K_{ij} g_j = \lambda g_i$, where the kernel K_{ij} is now symmetric and is given by

$$K_{ij} = \left[\frac{w_i w_j}{(p_i^2 + \varepsilon)(p_j^2 + \varepsilon)} \right]^{1/2} \frac{p_i p_j}{2\pi^2} \left[\frac{m_3}{\hbar^2} \right] V_\ell(p_i, p_j). \quad (12)$$

This matrix equation can be solved for the eigenvalue λ as a function of ε , using the same techniques as in previous work (Ghassib *et al.*, 1976; Bishop *et al.*, 1977). An infinite spectrum of λ will be obtained for a given ε (Mathews and Walker, 1969). However, the only relevant eigenvalue here is the *lowest*, i.e., the negative value of greatest absolute magnitude.

2.3 In ⁷Li vapor

Two many-body effects should now be incorporated into the picture. The first is the replacement of m with an effective atomic mass m^* ($> m$). This should lead to more

‘localization’ of the atoms and, hence, more binding. In the absence of concrete data on m^* , both experimental and theoretical, it is taken in the present low-density range as 1.1 m . The dependence of the resulting binding energy on m^* merits a thorough investigation; this will be attempted in a future work for Li and other atomic gases.

The second medium effect is an effective binary interaction V_{eff} . Again, in the absence of such an interaction in the literature, derived either from first principles or from semiempirical considerations, the following recipe is offered – based on heuristic arguments: In the short-range region, $V(r)$ is retained because it is so ‘stiff’, energetically speaking, as to be hardly affected by, say, the vapor chemical potential. Conversely, the long-range component, including the potential well, will become less attractive, judging from cumulative experience (Ghassib, 2019). We have, therefore, multiplied this component by a factor of 0.9. A more comprehensive investigation of V_{eff} for Li and other atomic vapors will again be attempted elsewhere.

3. Results and Discussion

In the same heuristic vein already mentioned, only the S-wave is considered in our present calculations. Our results are summarized in Tables 2-3 and Figs. 1-4. The curve in each figure represents $\lambda = \lambda(\varepsilon)$. Its intersection with the line $\lambda = -1$ gives the value of ε corresponding to the binding energy E_B .

Table 2, together with Figs. 1 and 2, represent E_B for the singlet and triplet states in free space. Table 3, together with Figs. 3 and 4, display the corresponding E_B in the vapor. The total binding energy E_B^T in each case is the weighted sum of the singlet $E_B^{(1)}$ and the triplet $E_B^{(3)}$:

$$E_B^T = \frac{1}{4}E_B^{(1)} + \frac{3}{4}E_B^{(3)}. \quad (13)$$

The free-space E_B^T agrees remarkably well with the experimental result of 6.150×10^3 K (Wheeler *et al.*, 2004), in light of all the above approximations. Unfortunately, no parallel result is available in the literature to compare to our E_B^T in the vapor, which (within the present scheme) is somewhat less (by 1.255×10^3 K) than its free-space counterpart.

Table 2: The S-wave binding energy E_B [K] of Li_2 molecules in free space.

Binding Energy, E_B [K] (Free Space)		
Singlet	Triplet	Total
2.2436×10^4	4.3263×10^2	5.933×10^3

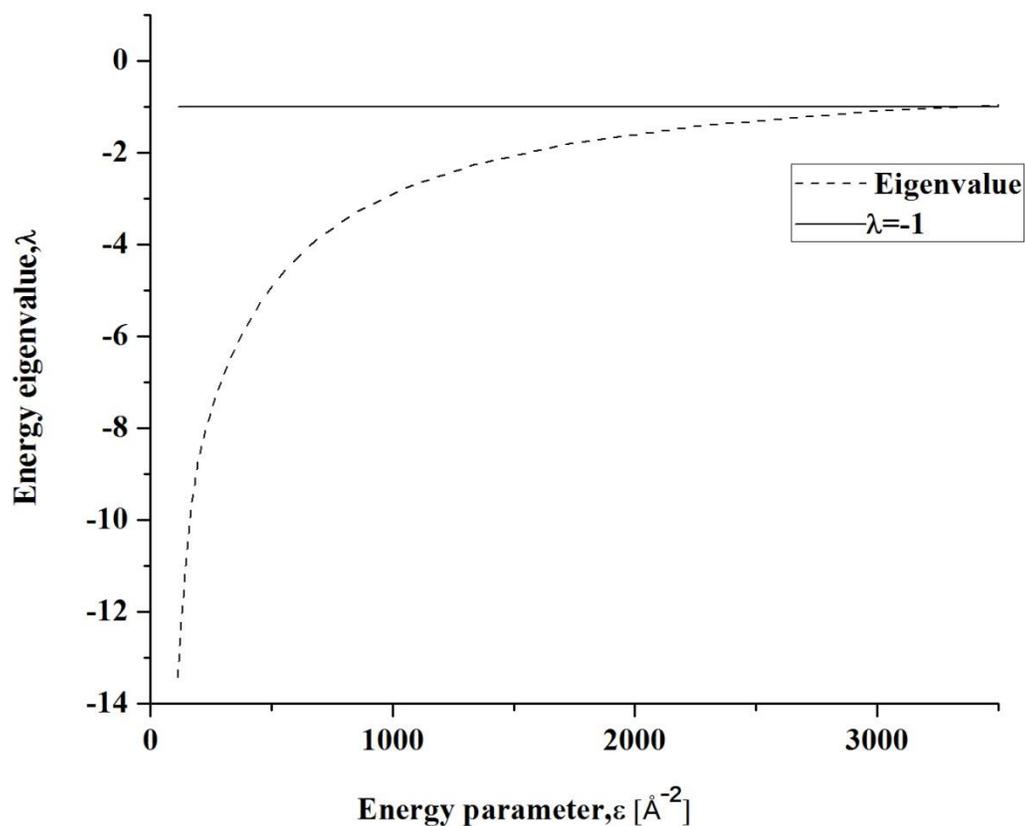


Figure 1: The S-wave eigenvalue λ for the singlet state, in free space, as a function of the energy parameter ε . The intersection with the line $\lambda = -1$ gives the corresponding binding energy.

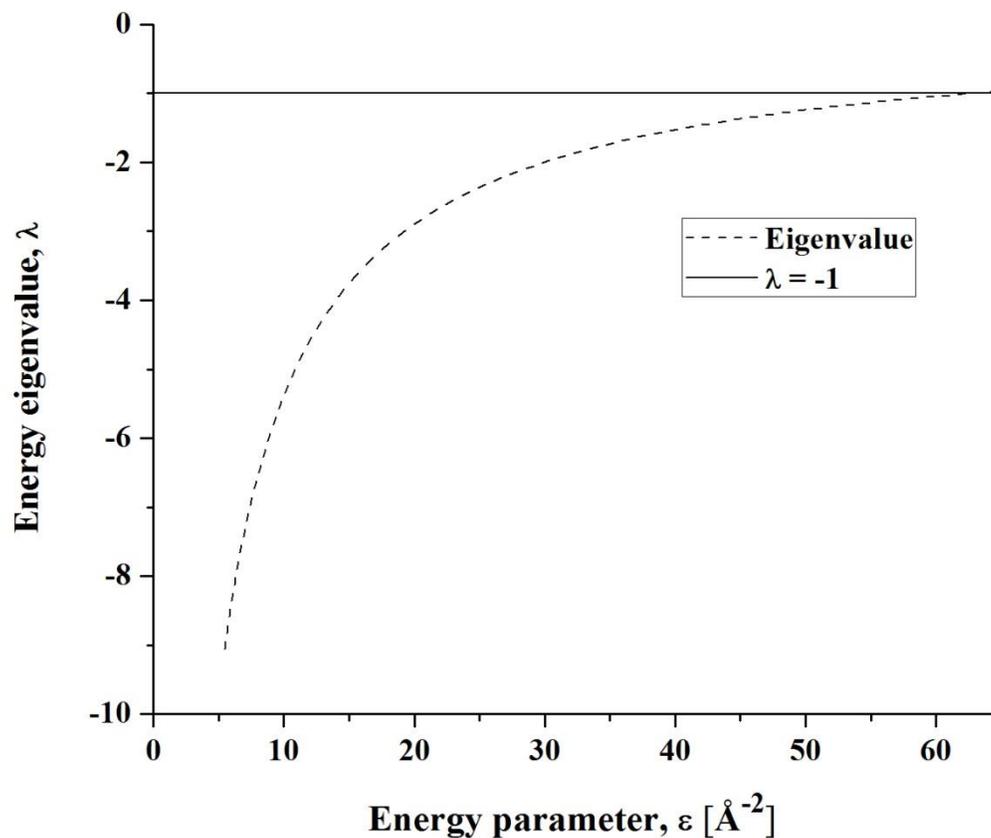


Figure 2: The S-wave eigenvalue λ for the triplet state, in free space, as a function of the energy parameter ε . The intersection with the line $\lambda = -1$ gives the corresponding binding energy.

Table 3: The S-wave binding energy E_B [K] of Li_2 molecules in the vapor.

Binding Energy, E_B [K] (Vapor)		
Singlet	Triplet	Total
1.7665×10^4	3.4909×10^2	4.678×10^3

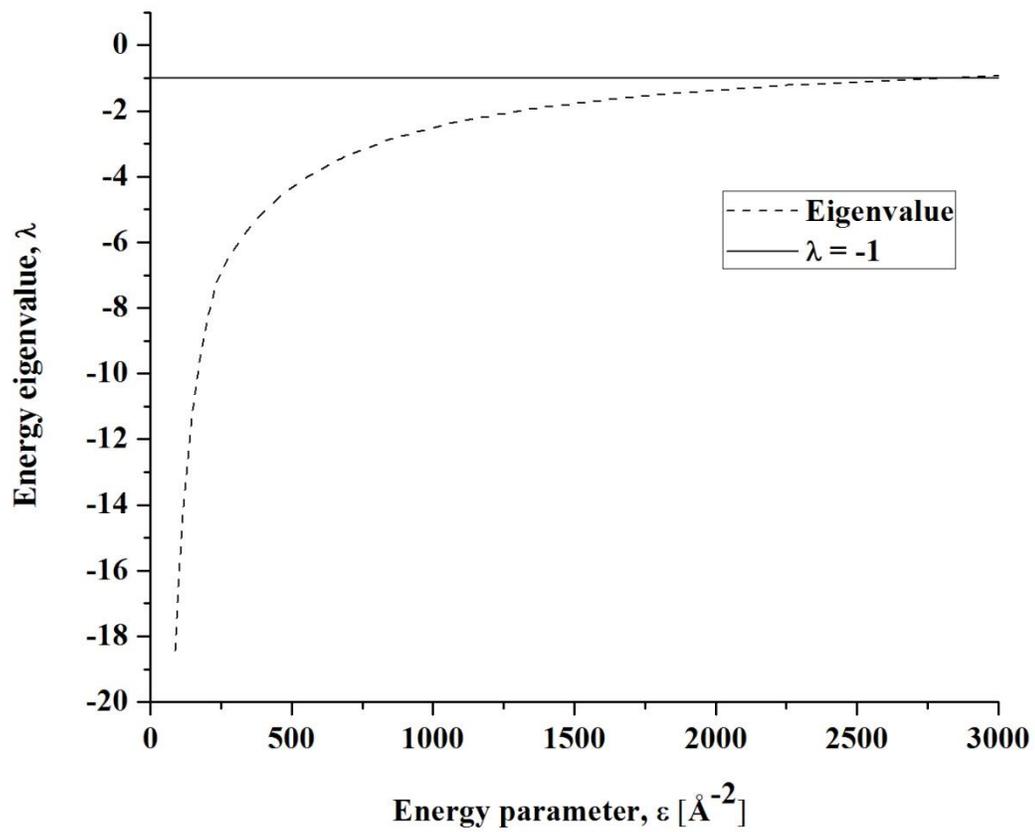


Figure 3: The S-wave eigenvalue λ for the singlet state, in the vapor, as a function of the energy parameter ϵ . The intersection with the line $\lambda = -1$ gives the corresponding binding energy.

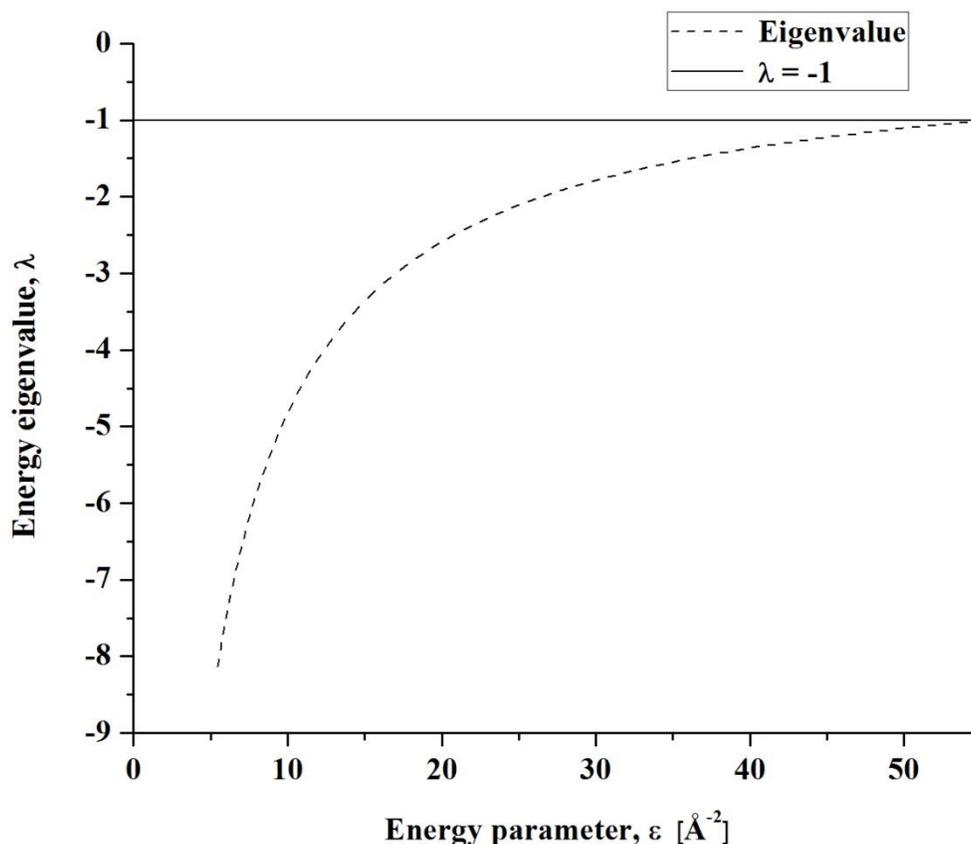


Figure 4: The S-wave eigenvalue λ for the triplet state, in the vapor, as a function of the energy parameter ε . The intersection with the line $\lambda = -1$ gives the corresponding binding energy.

4. Conclusion

The present work can be regarded as a preliminary calculation for the binding energy of ${}^7\text{Li}$ molecules in both free space and Li vapor. The next steps include the following, more elaborate calculations which are now in progress and will be published elsewhere: (1) Higher l -waves will be incorporated till convergence is attained. (2) A thorough exploration of the dependence of the vapor results on the effective mass and the effective interaction will be carried out. (3) Other alkali metal vapors will be considered.

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