

Non-Born–Oppenheimer study of positronic molecular systems: $e^+\text{LiH}$

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Very accurate non-Born–Oppenheimer variational calculations of the ground state of $e^+\text{LiH}$ have been performed using explicitly correlated Gaussian functions with preexponential factors dependent on powers of the internuclear distance. In order to determine the positron detachment energy of $e^+\text{LiH}$ and the dissociation energy corresponding to the $e^+\text{LiH}$ fragmentation into HPs and Li^+ we also calculated non-BO energies of HPs, LiH , and Li^+ . For all the systems the calculations provided the lowest ever-reported variational upper-bounds to the ground state energies. Annihilation rates of HPs and $e^+\text{LiH}$ were also computed. The dissociation energy of $e^+\text{LiH}$ into HPs and Li^+ was determined to be 0.036 548 hartree. © 2004 American Institute of Physics.
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I. INTRODUCTION

During the last several years very accurate methods for describing the coupled electron–nuclear motion in few-electron molecules have been developed in our laboratory.¹ Use of the explicitly one- and multi-center correlated Gaussian functions as the basis for the wave function expansion has been the centerpiece of the development. We have recently demonstrated that correlated Gaussian functions containing powers of the squared internuclear distance in the preexponential multiplier are capable of very precisely reproducing the vibrational excitations of small diatomic systems.^{2–4} The question that has arisen is whether one can use such basis functions in non-Born–Oppenheimer (non-BO) quantum mechanical calculations of molecular diatomic systems containing, besides electrons and nuclei, other particles. One example of such a particle is the positron. There has been considerable interest in the literature in small positronic systems such as HPs^{5–8} and $e^+\text{LiH}$.^{9–13} While calculations of the former system have not presented much difficulty using both finite-mass and infinite-mass approaches concerning the hydrogen nucleus, the calculations of $e^+\text{LiH}$ have appeared to be much more challenging particularly when methods going beyond the Born–Oppenheimer approximation were employed.¹¹ At the core of the difficulty encountered in Ref. 11, there has been the inability of simple spherical explicitly correlated Gaussians to describe the vibrational component of the non-BO wave function. Similar difficulties have appeared in non-BO calculations of conventional molecules.

To remedy the problem, we have implemented an explicitly correlated Gaussian basis set that contains preexponential factors in the form of powers of the internuclear distances.^{2–4} Such powers allowed us to very accurately represent the radial behavior of the non-BO wave function and describe the nuclear–nuclear correlation effects, which is crucial to achieving high accuracy in non-BO molecular calculations. Our calculations of the vibrational spectrum of H_2

demonstrated that even very highly excited states with a complicated node structure in the wave functions can be very well described using such basis functions. In the present work we test whether the basis can be applied in calculations of diatomic molecules containing positron. Our model system in the calculations is $e^+\text{LiH}$. The key question we address in this study is whether the explicitly correlated Gaussian basis with preexponential factor in the form of powers of the internuclear distance is capable of providing a proper representation for the positron–nucleus and positron–electron correlation effects in a diatomic system. The calculations of the HP system seem to indicate that, due to a small mass of the positron and a considerable overlap of the positron wave function with the function representing the nuclear motion, preexponential powers of the positron–nucleus distance do not need to be included in the basis functions. In the present calculations we verify whether this is also the case for $e^+\text{LiH}$.

Apart from the above-presented fundamental question concerning the basis set for non-BO calculations of positron molecules, the purpose of the present study is the very accurate determination of the positron detachment energy of $e^+\text{LiH}$ and the dissociation energy corresponding to the $e^+\text{LiH}$ fragmentation into HPs and Li^+ . Annihilation rates of HPs and $e^+\text{LiH}$ are also computed.

II. THE HAMILTONIAN

We begin with the full nonrelativistic Hamiltonian for the molecular system with the total number of particles (the electrons, the nuclei, and the positron) equal to $n + 1$. We place the system in the laboratory Cartesian coordinate system and write its total Hamiltonian so that no distinction is made between the electrons, the nuclei, and the positron by referring to $n + 1$ general particles with masses M_i , charges Q_i , and positions \mathbf{R}_i , where $i = 1, \dots, n + 1$:

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$$\hat{H}_{\text{tot}} = - \sum_{i=1}^{n+1} \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^{n+1} \sum_{j>i}^{n+1} \frac{Q_i Q_j}{R_{ij}}. \quad (1)$$

In Eq. (1), $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are interparticle distances. This Hamiltonian describes a system in which the motions of all particles are coupled. Next we make a transformation to separate the Hamiltonian representing the motion of the center of mass in the laboratory coordinate system from the internal Hamiltonian, $\hat{H}_{\text{int}} = \hat{H}$, thereby reducing the $(n+1)$ -particle problem to an n -pseudoparticle problem. If we choose to place a heavy particle (nucleus 1 with mass M_1) at the center of the internal Cartesian coordinate system, and define the internal coordinates of pseudoparticles as: $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$, the resulting internal Hamiltonian defined in terms of the coordinates \mathbf{r}_i is

$$\hat{H} = - \frac{1}{2} \left(\sum_i^n \frac{1}{m_i} \nabla_i^2 + \sum_{i \neq j}^n \frac{1}{M_1} \nabla_i' \nabla_j \right) + \sum_{i=1}^n \frac{q_0 q_i}{r_i} + \sum_{i < j}^n \frac{q_i q_j}{r_{ij}}, \quad (2)$$

where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ and the prime (') denotes vector/matrix transposition. This Hamiltonian describes a system containing a nucleus at the origin of the coordinates with charge $q_0 = Q_1$; also in the system there are n pseudoparticles, or internal particles, which are characterized by the reduced masses $m_i = M_1 M_{i+1} / (M_1 + M_{i+1})$ and charges $q_i = Q_{i+1}$. The second term in the parentheses is the mass polarization term, which arises from the coordinate transformation. In the potential energy term, r_i and r_{ij} are defined as: $r_i = |\mathbf{r}_i|$ and $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$. The eigenfunction of this Hamiltonian will be a function of the positions of all n pseudoparticles, meaning that all the particles forming the system, including the electron, the nuclei, and the positron, are described by the wave function.

For example, for $e^+ \text{LiH}$, the internal Hamiltonian describes the motions of six pseudoparticles in the central field of a lithium nucleus placed in the center of the coordinate system:

$$\hat{H} = - \frac{1}{2} \left(\sum_i^6 \frac{1}{m_i} \nabla_i^2 + \sum_{i \neq j}^6 \frac{1}{M_1} \nabla_i' \nabla_j \right) + \sum_{i=1}^6 \frac{q_0 q_i}{r_i} + \sum_{i < j}^6 \frac{q_i q_j}{r_{ij}}, \quad (3)$$

where M_1 is the mass of the lithium nucleus, $q_0 = 3$, $q_1 = 1$, $q_2 = q_3 = q_4 = q_5 = -1$, and $q_6 = 1$.

III. MASS VALUES

We used the following values for the nuclear masses in the calculations: $m_{\text{Li}} = 12\,786.393\,54 m_e$ (^7Li isotope), $m_{\text{H}} = 1836.152\,667\,5 m_e$ taken from Refs. 14 and 15, where m_e stands for the mass of the electron.

IV. BASIS SET AND MATRIX ELEMENTS

In our calculations we used a basis of explicitly correlated spherical Gaussians multiplied by powers of the internuclear distance. If we use \otimes to denote the Kronecker product of two matrices, the general form for these basis functions is given by

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \quad (4)$$

where \mathbf{r} is a $3n \times 1$ vector of the internal Cartesian coordinates of the pseudoparticles \mathbf{r}_i , L_k is an $n \times n$ lower triangular matrix of nonlinear variation parameters, I_3 is the 3×3 identity matrix, and r_1 is the internuclear distance. Raising this distance to powers m_k moves the maximum of the Gaussian away from the center of the coordinate system. Such an effect is desirable because the maximum probability of finding the second nucleus relative to the first one is around the equilibrium internuclear distance, which for the system studied in this work ranges between 2 and 4 bohrs. The Kronecker product with the identity matrix ensures that the basis functions are rotationally invariant and, hence, are eigenfunctions of the square of the angular momentum operator corresponding to the zero eigenvalue. Writing the matrix of nonlinear parameters in the Cholesky factored form as $L_k L_k'$ is a convenient way to ensure that the quadratic form in the Gaussian exponential is positively definite and, consequently, the square integrability of the basis functions is automatically ensured. The expressions for all basic matrix elements with basis functions (4), such as overlap, kinetic and potential energy, and their derivatives with respect to the nonlinear variational parameters, can be found in the previous work of our group.³ Here we only present the expression for the normalized matrix element of the delta function that depends on an interparticle distance, $\delta(\mathbf{r}_i - \mathbf{r}_j)$. It has the following form:

$$\frac{\langle \phi_k | \delta(\mathbf{r}_i - \mathbf{r}_j) | \phi_l \rangle}{\sqrt{\langle \phi_k | \phi_k \rangle \langle \phi_l | \phi_l \rangle}} = \frac{1}{\pi^{3/2}} \left(\frac{|A_{kl}|}{|D_{kl}|} \right)^{3/2} \left(\frac{(D_{kl}^{-1})_{11}}{(A_{kl}^{-1})_{11}} \right)^{(m_k + m_l)/2}, \quad (5)$$

where $A_{kl} = L_k + L_l$, A_{kl}^{-1} is the inverse of A_{kl} , and the vertical bars denote a determinant. Matrix D_{kl} is formed from matrix A_{kl} by adding the j th row to the i th row and the j th column to the i th column and then crossing out the j th column and row. Thus, matrix D_{kl} is the following $(n-1) \times (n-1)$ matrix:

$$D_{kl} = \begin{pmatrix} A_{1,1} & A_{1,2} & \cdots & A_{1,i} + A_{1,j} & \cdots & A_{1,j-1} & A_{1,j+1} & \cdots & A_{1,n} \\ A_{2,1} & A_{2,2} & \cdots & A_{2,i} + A_{2,j} & \cdots & A_{2,j-1} & A_{2,j+1} & \cdots & A_{2,n} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ A_{i,1} + A_{j,1} & A_{i,2} + A_{j,2} & \cdots & A_{i,i} + A_{i,j} + A_{j,i} + A_{j,j} & \cdots & A_{i,j-1} + A_{j,j-1} & A_{i,j+1} + A_{j,j+1} & \cdots & A_{i,n} + A_{j,n} \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots \\ A_{j-1,1} & A_{j-1,2} & \cdots & A_{j-1,i} + A_{j-1,j} & \cdots & A_{j-1,j-1} & A_{j-1,j+1} & \cdots & A_{j-1,n} \\ A_{j+1,1} & A_{j+1,2} & \cdots & A_{j+1,i} + A_{j+1,j} & \cdots & A_{j+1,j-1} & A_{j+1,j+1} & \cdots & A_{j+1,n} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ A_{n,1} & A_{n,2} & \cdots & A_{n,i} + A_{n,j} & \cdots & A_{n,j-1} & A_{n,j+1} & \cdots & A_{n,n} \end{pmatrix}. \quad (6)$$

Here we dropped indices kl denoting basis function numbers for the sake of clarity. Thus, $A_{1,1}$ should be read as $(A_{kl})_{1,1}$. By selecting the particular i and j in Eq. (5) one can obtain the average value of the delta function for a particular pair of the particles.

In accordance with the Pauli principle, the basis functions (4) must have proper permutational symmetry so that the product of the spatial and spin part is antisymmetric with respect to interchanging the electron labels. In this work the antisymmetrization was implemented using the standard approach based on Young operators (see, for example, Ref. 16).

V. RESULTS

It is well known that the convergence of variational expansions in terms of correlated Gaussians strongly depends on how one selects the nonlinear parameters in the Gaussian exponentials. In order to get high-accuracy results in the calculations, one needs to perform optimizations of those parameters at some level. Due to a usually large number of basis functions in non-BO calculations and, consequently, a large number of the exponential parameters, this task represents a serious computational problem. The two most commonly applied approaches to the parameter optimization are: a full optimization, which is very effective when the analytical gradient of the variational energy functional with respect to the parameters is available; and the method based on a stochastic selection of the parameters.

In the present calculations we applied a hybrid method that combines the gradient-driven optimizations with the stochastic selection method. In this approach we first generated a relatively small basis set for each of the studied systems using the full gradient optimization. This generated a good starting point for each system for the next step of the procedure. In this next step we applied the following strategy. We incrementally increased the size of the basis set by including additional basis functions one by one with randomly selected values of the nonlinear parameters and values of the preexponential powers. After including a function into the basis set, we first optimized the power of its preexponential factor using the finite-difference approach and then the nonlinear parameters in its exponent using the analytical-gradient approach. After adding several new basis functions using this approach (this number was 25 in most cases) the whole basis

was being reoptimized by means of the gradient approach applied consecutively to each basis function, one function at a time. This continued until the number of basis functions reached 3200 for each of the considered systems. 3200 was just a practical limit of the number of functions that provided an acceptable level of convergence of the energy for each of the considered systems and was feasible from the point of view of the computational power available for the calculations. Although this procedure has been proven to be quite efficient in optimizations of large basis sets of correlated Gaussians, it still requires a lot of computational resources, especially for systems with a larger number of particles and a large number of particle permutations in the Young symmetry operators. To overcome this problem, the code we used was extensively parallelized for use on a multinode computational system. For this purpose we used the Message Passing Interface (MPI) and we were able to achieve sufficient parallelization level of the code for runs with 8–12 processors per task. This development enabled us to optimize relatively large basis sets. The calculations were carried out on a Linux Beowulf cluster at the University of Arizona Center of Computing and Information Technology.

The convergence of the energy values for HPs, LiH, and $e^+ \text{LiH}$ in terms of the number of the basis functions is shown in Table I. In the case of LiH and $e^+ \text{LiH}$ the powers m_k in Eq. (4) were selected from the interval of 0–200 and only even values were used. The obtained distribution of m_k 's had a mean value of 67.5 and the standard deviation of 48.3 for LiH. The corresponding numbers for $e^+ \text{LiH}$ were 80.8 and 52.8. The higher mean value of the powers for $e^+ \text{LiH}$ than for LiH can be explained by the longer equilibrium distance of the former, which requires that the maxi-

TABLE I. Total non-BO energy in hartrees as a function of basis size.

| N | HPs | LiH | $e^+ \text{LiH}$ |
|------|------------------|----------------|------------------|
| 800 | -0.788 870 504 0 | -8.066 278 419 | -8.103 075 429 |
| 1200 | -0.788 870 639 8 | -8.066 344 535 | -8.103 905 788 |
| 1600 | -0.788 870 679 0 | -8.066 382 950 | -8.104 256 550 |
| 2000 | -0.788 870 694 0 | -8.066 404 077 | -8.104 478 249 |
| 2400 | -0.788 870 701 4 | -8.066 415 542 | -8.104 598 552 |
| 2800 | -0.788 870 705 7 | -8.066 423 527 | -8.104 683 502 |
| 3200 | -0.788 870 706 6 | -8.066 427 866 | -8.104 739 913 |

imum of the non-BO wave function in terms of the r_1 coordinate is shifted to higher values. This shifting for Gaussians is achieved by increasing the m_k values in the $r_1^{m_k}$ factors. Although a positronium hydride wave function can be obtained with very high precision even without using powers of the hydrogen–positron distance in the preexponential factors in the basis functions, we did include some functions with small preexponential powers (from 0 to 10) to ensure better numerical stability in the calculations. The calculation of HPs requires much fewer computational resources in comparison with those of LiH or e^+ LiH and including preexponential factors does not represent any problem.

The only previous attempt to calculate non-BO ground state energy of e^+ LiH was made in Ref. 11. In that work the authors used a 580-term set of explicitly correlated Gaussians without preexponential factors. Although the basis consisting of such functions is, in principle, complete, it reveals a very slow convergence rate in the case when there is more than one heavy particle in the system under consideration. As a result, the energy of $-8.089\,001\,0$ hartree obtained in Ref. 11 was far from being converged. For comparison, for the same basis size, 580 functions, in our calculations we obtained a significantly lower energy value equal to $-8.102\,073\,4$ hartree.

From the lowest energy values shown in Table I one can determine that the positron detachment energy of e^+ LiH, $PDE = E(e^+\text{LiH}) - E(\text{LiH})$, is $0.038\,312$ hartree. The lowest-energy fragmentation of e^+ LiH corresponds to dissociation of the system into HPs+Li $^+$. To calculate the dissociation energy, $DE = E(e^+\text{LiH}) - E(\text{Li}^+) - E(\text{HPs})$, one needs to determine the total energy of the Li $^+$ ion. Since the non-BO calculation of this quantity is very simple, rather than taking it from the literature, we recalculated it using our method. A 400-term expansion was sufficient to obtain a highly accurate result of $-7.279\,321\,518$ hartree, where, we believe, all the significant figures shown are exact. In the work of Mitroy and Ryzhikh,¹¹ we found the value of the Li $^+$ ground state energy of $-7.279\,325$ hartree. We think that the difference in the last digit of the result quoted by Mitroy and Ryzhikh and the energy obtained in our calculation results from the difference in the mass of the Li nuclei of $12\,863.2m_e$ used by them and the value of $m_{\text{Li}} = 12\,786.393\,54m_e$ used in our calculations.

Given the values of the HPs and Li $^+$ energies calculated in this work in addition to that of e^+ LiH, our dissociation energy is $0.036\,548$ hartree. This value qualitatively agrees with the value of $0.0382(2)$ hartree obtained in the Born–Oppenheimer calculations by Mella and co-workers¹² using the Quantum Monte Carlo method. It also agrees with the Born–Oppenheimer result of $0.036\,936$ obtained by Strasburger¹⁰ with the use of explicitly correlated Gaussians and the variational method.

The lowest variational energy upper-bound for the Born–Oppenheimer LiH ground state energy to date is $-8.070\,538$ hartree.¹⁷ Assuming that the energies of Li and H with infinitely heavy nuclei are $-7.478\,060\,3$ ¹⁸ and -0.5 hartree respectively, one obtains the infinite-mass dissociation energy of LiH of $-0.092\,477\,7$ hartree. The finite-mass energy of LiH can be estimated by subtracting this number

TABLE II. Expectation values of the Li–H internuclear distance, its square, and electron–positron contact densities evaluated at $N=3200$ function basis size. All quantities in atomic units.

| System | $\langle r_{\text{LiH}} \rangle$ | $\langle r_{\text{LiH}}^2 \rangle$ | $\langle \delta(\mathbf{r}_{e^-e^+}) \rangle$ |
|-----------|----------------------------------|------------------------------------|---|
| HPs | ... | ... | $2.448\,55 \times 10^{-2}$ |
| LiH | 3.061 05 | 9.419 77 | ... |
| e^+ LiH | 3.444 70 | 11.939 7 | $7.088\,79 \times 10^{-3}$ |

from the sum of the finite-mass energies of Li and H atoms and by adding to the result the zero-point LiH energy. Using the finite-mass energy of Li of $-7.477\,451\,9$ hartree which one can calculate by using the expansion from the paper of Yan and Drake,¹⁸ the corresponding value for the H atom of $-0.499\,727\,8$ hartree, and the zero-point LiH energy of $0.003\,198\,1$ Hartree (see Ref. 19) we obtain the LiH ground state energy corrected for the finite nuclear masses equal to $-8.066\,459$ hartree. The use of experimentally determined zero-point energy of $-0.003\,179\,9$ ²⁰ shifts this value to $-8.066\,478$ hartree. The difference between this value and our non-BO result of $-8.066\,427\,866$ hartree is larger than the estimated sum of their inaccuracies. Although, perhaps, this may partially be attributed to relatively low accuracy of the zero-point energy, it is clear that the nonadiabatic effect of the coupled electron–nuclear motion must play a role in the difference.

In Table II we present expectation values of the internuclear distance and its square for LiH and e^+ LiH as well as the electron–positron contact densities for HPs and e^+ LiH evaluated with the largest basis set of 3200 basis functions obtained in the calculations. It should be noted that the mean internuclear distance of LiH calculated here is slightly higher than the known value, 3.015 bohr, of the equilibrium nuclear distance, i.e., the distance where the potential energy curve reaches its minimum. This is, obviously, an expected result since larger distances contribute more to the mean distance when one averages the internuclear distance over the “vibrational” part of the wave function. For e^+ LiH our r_{LiH} ($\equiv r_1$) mean distance of 3.445 bohr agrees well with the equilibrium internuclear separation of 3.348 bohr obtained by Strasburger¹⁰ in the Born–Oppenheimer calculations. However, the Quantum Monte Carlo calculations of Mella *et al.*¹² gave an unexpectedly large internuclear distance of 3.458 bohr. It is possible, that, perhaps, this was due to rather long distance between the points where the potential energy curve was computed and a relatively high “numerical noise” in energies.

An important characteristic of positronic systems relevant to the experiment is their lifetimes. The expectation value of the electron–positron contact density allows one to evaluate the two-photon annihilation rate for a positronic system using

$$\Gamma_{2\gamma} = n \frac{\pi \alpha^4 c}{a_0} \langle \delta(\mathbf{r}_{e^-e^+}) \rangle,$$

where α is the fine structure constant, a_0 is the Bohr radius, c is the velocity of light, and n denotes the number of electron–positron pairs in the system (2 and 4 in the case of

HPs and e^+LiH , respectively). The two-photon annihilation rates we obtained in the present calculations are: $2.4716 \times 10^9 \text{ s}^{-1}$ for HPs, $1.4311 \times 10^9 \text{ s}^{-1}$ for e^+LiH . This indicates that a positron attached to LiH survives much longer than in the HP system. The HP annihilation rate can be compared with the result of Yan and Ho obtained in a finite-mass calculation using Hylleraas coordinates²¹ (HPs) and with the explicitly correlated Gaussian calculation⁷ performed for $^\infty\text{HPs}$ (HPs with infinitely heavy proton) which both yielded the value of $2.4722 \times 10^9 \text{ s}^{-1}$. In the case of e^+LiH we can again make a comparison with the Born–Oppenheimer Quantum Monte Carlo result of Mella and co-workers¹³ that yielded $1.49 \times 10^9 \text{ s}^{-1}$ (the vibrationally averaged result) and with the Born–Oppenheimer explicitly correlated Gaussian result of Strasburger¹⁰ where the value of $1.375 \times 10^9 \text{ s}^{-1}$ was obtained at the e^+LiH equilibrium distance of $R = 3.348 \text{ bohr}$.

Although our values for the electron–positron contact densities are probably the most precise ones obtained to date, their accuracy is somewhat worse than the accuracy of the energy or the mean distances. This is a usual difficulty that occurs when one uses Gaussian basis functions. Since these functions do not have terms proportional to the first power of the electron–positron distance in their Taylor expansion in the vicinity of the point $r_{e^-e^+} = 0$, they tend to converge slower for the expectation values where small interparticle distances weight much more than larger ones, as in the case of the electron–positron contact density.

VI. SUMMARY

In this work we applied explicitly correlated Gaussians with preexponential factors dependent on powers of the internuclear distance to a diatomic system containing a positron. The results show that these functions can be successfully used in such calculations. Very accurate, the best to date, ground state energies were obtained for HPs, LiH, and

e^+LiH without assuming the Born–Oppenheimer approximation. The key point that allowed us to obtain high precision results was the combination of stochastic selection of the basis functions with the use of the analytical gradient for optimization of nonlinear parameters. We calculated the two-photon annihilation rates for HPs and e^+LiH in the ground state. In future studies of e^+LiH it would be interesting to consider vibrationally excited states. The states that lie close to the dissociation limit may have annihilation rates that differ significantly from the ground state. The nonadiabatic effects in such states may play a more significant role than in the ground state. However, the non-BO consideration of highly vibrationally excited states of e^+LiH represents a level of difficulty that exceeds the computational power available to us at present time.

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