

Relativistic calculations using Monte Carlo methods: One-electron systems

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Variance minimization and Monte Carlo integration are used to evaluate the four-component Dirac equation for a number of one-electron atomic and diatomic systems. This combination produces accurate energies, is relatively simple to implement, and exhibits few of the problems associated with traditional techniques. [S1063-651X(99)09709-3]

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I. INTRODUCTION

In a series of earlier papers, we used the variational Monte Carlo method to compute the total energy,

$$\langle H \rangle = \frac{\sum_i [\Psi_i H \Psi_i / w_i]}{\sum_i [\Psi_i^2 / w_i]}, \quad (1)$$

and variance,

$$\sigma^2 = \frac{\sum_i [(H \Psi_i - E_{in} \Psi_i)^2 \Psi_i^2 / w_i^2]}{\left\{ \sum_i [\Psi_i^2 / w_i] \right\}^2}, \quad (2)$$

of several nonrelativistic atomic and molecular systems [1–9]. Here H is the usual nonrelativistic Hamiltonian, $\Psi_i = \Psi_i(\mathbf{x}_i)$ is the value of the trial wave function at the Monte Carlo integration point, \mathbf{x}_i , $w_i = w(\mathbf{x}_i)$ is the relative probability of choosing this point, and E_{in} is a reference energy which is fixed at a value close to the desired state. As in all Monte Carlo calculations, Eq. (2) is proportional to \mathbf{c}/\sqrt{N} , where N is the number of integration points and \mathbf{c} is a constant which depends on the trial wave function [5–9] and on how one chooses the integration points [7,9]. Because \mathbf{c} is

zero for an exact eigenfunction, the best trial wave function can be defined to be that which minimizes the variance in $\langle H \rangle$ [2,8].

Aissing was the first to show that variance minimization could also be applied to relativistic systems [10]. He examined a one-electron atom using the two-component Dirac equation and obtained excellent results. In this paper we extend this work to the four-component Dirac equation. This will allow us to examine both atomic and molecular systems. Section II contains a detailed description of how Monte Carlo can be used to compute the total energy of a one-electron atom. Because the exact eigenfunction and eigenvalue of this system are known, this calculation provides a necessary test of our method. In Sec. III, we examine the diatomic systems H_2^+ and its $Z=90$ analog, Th_2^{179+} , using several nonexact trial wave-function forms. Although the energy of both systems has recently been determined using a number of methods [11–20], our Monte Carlo calculations provide a completely independent method of evaluating these energies. Unless otherwise indicated, all values in this paper are given in atomic units and $c = 137.03602$.

II. ATOMIC CALCULATIONS

Given the four-component Dirac equation

$$H_D \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = \begin{bmatrix} V+c^2 & 0 & ic \frac{d}{dz} & \left(-ic \frac{d}{dx} - c \frac{d}{dy}\right) \\ 0 & V+c^2 & \left(-ic \frac{d}{dx} + c \frac{d}{dy}\right) & -ic \frac{d}{dz} \\ ic \frac{d}{dz} & \left(-ic \frac{d}{dx} - c \frac{d}{dy}\right) & V-c^2 & 0 \\ \left(-ic \frac{d}{dx} + c \frac{d}{dy}\right) & -ic \frac{d}{dz} & 0 & V-c^2 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix} = E \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \end{bmatrix}, \quad (3)$$

the relativistic energy can be computed by

$$\langle H_D \rangle = \frac{\sum_i [u_1^*(i) H_D u_1(i) + u_2^*(i) H_D u_2(i) + u_3^*(i) H_D u_3(i) + u_4^*(i) H_D u_4(i)] / w_i}{\sum_i [|u_1(i)|^2 + |u_2(i)|^2 + |u_3(i)|^2 + |u_4(i)|^2] / w_i} \quad (4)$$

TABLE I. Orbital energies (in a.u.) of H_2^+ ($R_{AB} = \pm 1$) computed using three different wave-function forms. Our results were computed using 4000 integration points.

No. of functions	Slater [Eq. (8)]	Gaussian [Eq. (9)]	Mixed [Eq. (10)]
1	$-1.055\,456 \pm 0.003\,185$	$-1.108\,468 \pm 0.002\,989$	$-1.101\,419 \pm 0.000\,987$
2	$-1.101\,064 \pm 0.001\,167$	$-1.098\,842 \pm 0.001\,504$	$-1.103\,043 \pm 0.000\,343$
3	$-1.100\,923 \pm 0.000\,651$	$-1.099\,974 \pm 0.001\,007$	$-1.102\,703 \pm 0.000\,220$
4	$-1.099\,479 \pm 0.000\,524$	$-1.102\,085 \pm 0.000\,830$	$-1.102\,518 \pm 0.000\,146$
5	$-1.102\,863 \pm 0.000\,225$		$-1.102\,555 \pm 0.000\,097$
6	$-1.102\,629 \pm 0.000\,180$		$-1.102\,479 \pm 0.000\,071$
7	$-1.102\,600 \pm 0.000\,145$		
8	$-1.102\,436 \pm 0.000\,090$		

and its variance by

$$\sigma^2 = \frac{\sum_i [|\Delta_1(i)|^2 + |\Delta_2(i)|^2 + |\Delta_3(i)|^2 + |\Delta_4(i)|^2] / w_i^2}{\{\sum_i [|u_1(i)|^2 + |u_2(i)|^2 + |u_3(i)|^2 + |u_4(i)|^2] / w_i \}^2}. \quad (5)$$

Here $u_p(i) = u_p(\mathbf{x}_i)$ and $\Delta_p(i) = u_p^*(\mathbf{x}_i) H_D u_p(\mathbf{x}_i) - E_{in} u_p^*(\mathbf{x}_i) u_p(\mathbf{x}_i)$ for $p=1,2,3,4$. Because the individual components can be complex, all complex conjugation is shown explicitly.

For the $1S_{1/2}$ state of a one-electron atom ($V = -Z/r$), we choose the trial wave-function form

$$\begin{aligned} u_1 &= \sum_k a_k r^\gamma \exp(-\alpha_k r), \\ u_2 &= 0.0, \\ u_3 &= \sum_k b_k r^\gamma \exp(-\alpha_k r) i z / r, \\ u_4 &= \sum_k c_k r^\gamma \exp(-\alpha_k r) (y + ix) / r. \end{aligned} \quad (6)$$

Using a set of 4000 integration points, we minimized Eq. (5) with respect to the adjustable parameters γ , α_1 , b_1 , and c_1 (here we set $a_1 = 1.0$ for normalization purposes). The integration points, \mathbf{x}_i , and their weights, w_i , were chosen ‘‘biased as random’’ [5–9] from the importance function $\exp(-r/Z)$. This function is more diffuse than the expected wave function and so it should adequately sample the space. For $Z=92$ our method yields an energy of $-4861.197\,645$ with a statistical error equal to the machine precision of our computer. This result is in excellent agreement with the exact value [21,22] and demonstrates that variance minimization is able to determine the exact coefficients,

$$\begin{aligned} \gamma &= -1 + (1 - Z^2/c^2)^{1/2}, \\ \alpha_1 &= Z, \\ a_1 &= 1, \\ b_1 &= -\gamma c, \\ c_1 &= \gamma c, \end{aligned} \quad (7)$$

even when an arbitrary set of parameters is used as a starting point. The situation in which the exact trial wave-function form is able to reproduce the exact eigenfunction is a necessary test that variance minimization passes.

III. DIATOMIC CALCULATIONS

For the $1S_{1/2}$ state of a one-electron homonuclear diatomic ($V = -Z_A/|R_A - r| - Z_B/|R_B - r|$), no exact trial wave-function form exists. For this reason we have examined a variety of forms in order to determine what features will give the fastest convergence. The first form is

$$\begin{aligned} u_1 &= \sum_k a_k [r_A^\gamma \exp(-\alpha_k r_{Ak}) + r_B^\gamma \exp(-\alpha_k r_{Bk})], \\ u_2 &= 0.0, \\ u_3 &= \sum_k b_k [r_A^\gamma \exp(-\alpha_k r_{Ak}) i(z - R_A)/r_A \\ &\quad + r_B^\gamma \exp(-\alpha_k r_{Bk}) i(z - R_B)/r_B], \\ u_4 &= \sum_k c_k [r_A^\gamma \exp(-\alpha_k r_{Ak}) (y + ix)/r_A \\ &\quad + r_B^\gamma \exp(-\alpha_k r_{Bk}) (y + ix)/r_B], \end{aligned} \quad (8)$$

where

$$\begin{aligned} r_A^2 &= x^2 + y^2 + (z - R_A)^2, & r_{Ak}^2 &= x^2 + y^2 + (z - \delta_k)^2, \\ r_B^2 &= x^2 + y^2 + (z - R_B)^2, & r_{Bk}^2 &= x^2 + y^2 + (z + \delta_k)^2, \end{aligned}$$

and where $R_A = -R_B$ are the positions of the two nuclei on the z axis. This form was chosen in part because it has the correct behavior at infinity and at each nucleus. It is the relativistic representation of a molecular orbital composed of atomic orbitals as described, for example, in Eyring, Walter, and Kimball [23]. Since the position of each Slater, δ_k , can be optimized along the z axis, a small number of terms should capture a large percentage of the orbital energy. As shown in Tables I and II, this is indeed the case.

TABLE II. Orbital energies (in a.u.) of Th_2^{179+} ($R_{AB} = \pm 1/90$) computed using three different wave-function forms. Our results were computed using 4000 integration points.

No. of functions	Slater [Eq. (8)]	Gaussian [Eq. (9)]	Mixed [Eq. (10)]
1	-9356 ± 35	-9535 ± 26	-9480 ± 10
2	-9154 ± 25	-9464 ± 14	-9495 ± 4
3	-9486 ± 9	-9479 ± 8	-9496 ± 3
4	-9483 ± 6	-9482 ± 7	-9498 ± 2
5	-9495 ± 2		-9499 ± 1
6	-9498 ± 2		-9498 ± 1
7	-9498 ± 1		
8	-9497 ± 1		

For our second trial wave-function form, we used a typical Gaussian-type function,

$$\begin{aligned}
 u_1 &= \sum_k a_k [r_A^\gamma \exp(-\alpha_k r_{Ak}^2) + r_B^\gamma \exp(-\alpha_k r_{Bk}^2)], \\
 u_2 &= 0.0, \\
 u_3 &= \sum_k b_k [r_A^\gamma \exp(-\alpha_k r_{Ak}^2) i(z - R_A)/r_A \\
 &\quad + r_B^\gamma \exp(-\alpha_k r_{Bk}^2) i(z - R_B)/r_B], \\
 u_4 &= \sum_k c_k [r_A^\gamma \exp(-\alpha_k r_{Ak}^2) (y + ix)/r_A \\
 &\quad + r_B^\gamma \exp(-\alpha_k r_{Bk}^2) (y + ix)/r_B].
 \end{aligned} \tag{9}$$

This form is much more short ranged than the one in Eq. (8), which is an important feature for describing bonding but it also has the wrong asymptotic behavior. As a result, the convergence is relatively slow as shown in Tables I and II.

In order to combine the best qualities of the two previous trial wave functions, we next tried the form

$$\begin{aligned}
 u_1 &= a [r_A^\gamma \exp(-\alpha r_A) + r_B^\gamma \exp(-\alpha r_B)] \\
 &\quad + \sum_k a_k [r_A^\gamma \exp(-\alpha_k r_{Ak}^2) + r_B^\gamma \exp(-\alpha_k r_{Bk}^2)], \\
 u_2 &= 0.0, \\
 u_3 &= b [r_A^\gamma \exp(-\alpha r_A) i(z - R_A)/r_A \\
 &\quad + r_B^\gamma \exp(-\alpha r_B) i(z - R_B)/r_B] \\
 &\quad + \sum_k b_k [r_A^\gamma \exp(-\alpha_k r_{Ak}^2) i(z - R_A)/r_A \\
 &\quad + r_B^\gamma \exp(-\alpha_k r_{Bk}^2) i(z - R_B)/r_B], \\
 u_4 &= c [r_A^\gamma \exp(-\alpha r_A) (y + ix)/r_A \\
 &\quad + r_B^\gamma \exp(-\alpha r_B) (y + ix)/r_B] \\
 &\quad + \sum_k c_k [r_A^\gamma \exp(-\alpha_k r_{Ak}^2) (y + ix)/r_A \\
 &\quad + r_B^\gamma \exp(-\alpha_k r_{Bk}^2) (y + ix)/r_B].
 \end{aligned} \tag{10}$$

Here a single Slater function is fixed on each atom to provide the correct asymptotic behavior and a set of floating Gaussians is then arranged symmetrically with respect to each nucleus to describe the bonding. As shown in Tables I and II, the results from this form converge faster than either of the earlier trial wave-function forms.

To do all the optimizations described above, we generated a set of 4000 integration points from the importance function $\exp(-r/Z)$ and then minimized the variance with respect to all adjustable parameters (γ , α_k , a_k , b_k , c_k , and δ_k , where we set $a_1 = 1.0$ for normalization purposes). These parameters were then used to evaluate Eqs. (1) and (2) with a set of

TABLE III. Comparison of Monte Carlo orbital energies (in a.u.) and values obtained using other methods. Our results were computed using the mixed wave-function form [Eq. (10)] and 1 024 000 integration points.

No. of functions	H_2^+ ($R_{AB} = \pm 1$)	Th_2^{179+} ($R_{AB} = \pm 1/90$)
1	$-1.100\,756 \pm 0.000\,064$	-9469.78 ± 0.70
2	$-1.103\,068 \pm 0.000\,022$	-9495.37 ± 0.26
3	$-1.102\,789 \pm 0.000\,014$	-9493.69 ± 0.19
4	$-1.102\,677 \pm 0.000\,008$	-9497.46 ± 0.11
5	$-1.102\,668 \pm 0.000\,005$	-9497.86 ± 0.07
6	$-1.102\,658 \pm 0.000\,005$	-9497.37 ± 0.07
Extrapolation	$-1.102\,565 \pm 0.000\,011$	-9498.98 ± 0.32
Gaussian basis [11]	$-1.101\,31$	-9496.04
Finite element [12]	$-1.102\,481$	-9476.6
Min/Max [13]	$-1.102\,641\,581$	
Pert. theory [14]	$-1.102\,641\,6$	-9495.939
Finite element [15]	$-1.102\,641\,581$	
Gaussian basis [16]		$-9504.756\,696$
Pert. theory [17]		$-9504.756\,7155$
Min/Max [18]		-9504.7497

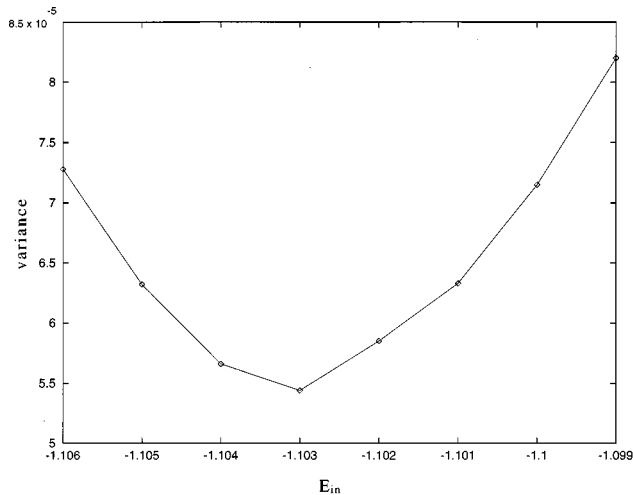


FIG. 1. Variance of H_2^+ as a function of the input energy. The variance was obtained from the optimization of a six-term mixed wave function [Eq. (10)] using 4000 configurations.

1 024 000 integration points. This latter step was performed in order to insure complete statistical independence with the original set of points. In Table III we list the resulting orbital energies and their variances as a function of the number of basis functions. These values show a rapid decrease in the variance as more basis functions are added to the trial wave function. To obtain an estimate of the energy and variance that this wave-function form would produce with an infinite number of basis functions, we can take these values and extrapolate to zero Monte Carlo error. This procedure (which is described in detail in Appendix A) produces a value of $\langle H_D \rangle = -1.102\,565 \pm 0.000\,11$ for H_2^+ . When this same procedure is applied to Th_2^{179+} we get an extrapolated value of $\langle H_D \rangle = -9498.98 \pm 0.32$. Both of these energies are in good agreement with those determined using other methods [11–20] but they are also somewhat higher than the best available estimates. This suggests that our wave-function form could still be improved.

One obvious difference between the H_2^+ and Th_2^{179+} calculations is that the former converges from below while the

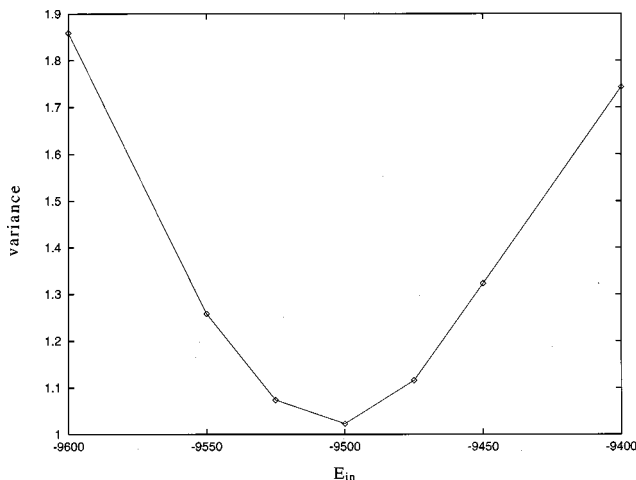


FIG. 2. Variance for Th_2^{179+} as a function of the input energy. The variance was obtained from the optimization of a six-term mixed wave function [Eq. (10)] using 4000 configurations.

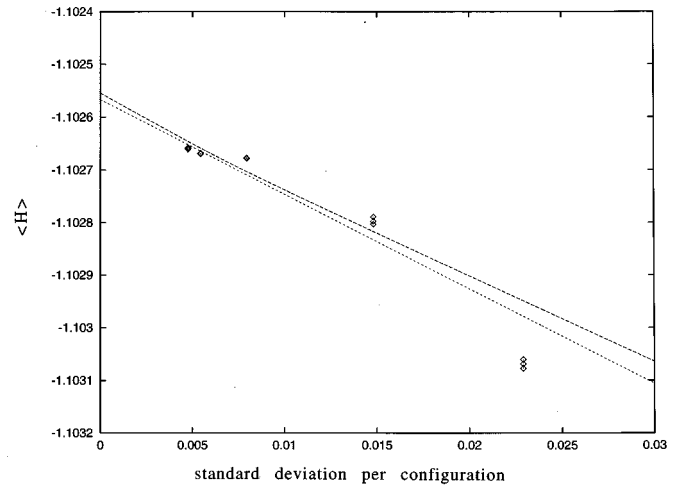


FIG. 3. Extrapolation of our H_2^+ energies as a function of the standard deviation per configuration. All values were computed using 1 024 000 configurations. The two lines denote the upper and lower bounds of the fit.

latter converges from above. The question of whether our result is variational is not a simple one. When the variance of $\langle H_D \rangle$ is greater than the variance of the potential, spurious minima in the variance can occur when the small components of the wave function are zero. In such a case the kinetic energy of the entire system is zero and the expectation value of $\langle H_D \rangle$ is not bounded. When this occurs, $\langle H_D \rangle$ can be optimized to almost any energy. When the variance in $\langle H_D \rangle$ is substantially less than the variance in $\langle V \rangle$, the kinetic energy coming from the small components plays its proper role of canceling the variation in the potential and $\langle H_D \rangle$ become accurate in the sense that it gives a meaningful value that can be extrapolated to zero variance. A more rigorous version of this argument is given in Appendix B.

To verify that our diatomic wave functions have not been optimized to some erroneous state, we have plotted the variance as a function of E_{in} . If our calculations are converging to a clear unique representation of the true eigenfunction,

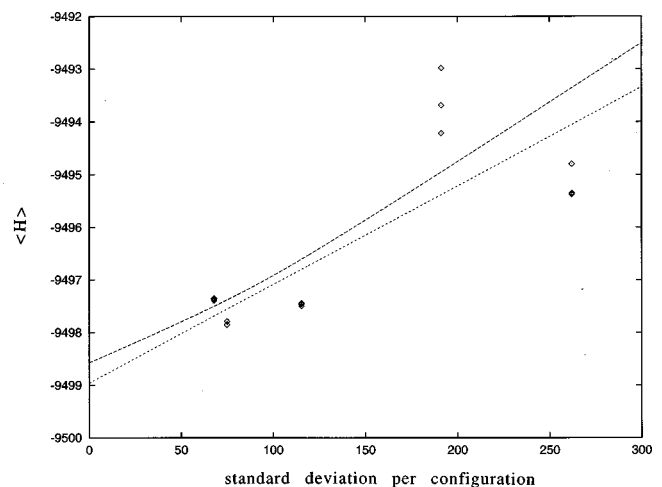


FIG. 4. Extrapolation of our Th_2^{179+} energies as a function of the standard deviation per configuration. All values were computed using 1 024 000 configurations. The two lines denote the upper and lower bounds of the fit.

then this graph should have single minimum at the true eigenvalue. As Figs. 1 and 2 show, this is indeed the case. In the case of energy-minimization methods, the energy can be obtained by the selected addition of positive and negative energy states. This often leads to spurious solutions. Although such occurrences are thought to be minimized by using balanced basis sets, we avoid this question altogether by not using an energy-based method.

IV. CONCLUSIONS

We have described how one-electron relativistic calculations can be performed using the Monte Carlo method. By using the fact that the variance of the relativistic energy must be zero for an eigenfunction, we can optimize the parameters in a trial wave-function form so as to minimize this quantity. Because this optimization does not directly depend on the relativistic energy, our Monte Carlo calculations provide a completely independent method of evaluating atomic, diatomic, and polyatomic systems.

In most ways the relativistic calculations presented here are very similar to their nonrelativistic counterparts. For this reason it should be quite straightforward to determine a number of properties from our wave functions [9]. The addition of the Breit interaction and other terms to the Hamiltonian (e.g., electric and magnetic fields) should also be straightforward. The extension of this method to systems with more than one electron is in progress.

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APPENDIX A: OBTAINING AN ENERGY ESTIMATE BY EXTRAPOLATION

The eigenvalue which solves the Dirac equation is the relativistic energy. There are two reasons why the expectation value of the Hamiltonian with a given trial function can be above or below this value. The first is an error that comes from using only a limited number of configurations to estimate the expectation value. This quantity, the variance, can be reduced by using a large number of configurations. The second error is due to the use of an inexact trial wave function. In any Monte Carlo calculation the standard deviation per configuration (a quantity related to the variance) becomes zero only when an exact trial wave function is used. This quantity can be reduced by using a better trial wave-function form or possibly by adding additional flexibility to the current trial wave function. In our calculations the size of the first error is small relative to the second because of the large number of configurations used. We were able to estimate the size of the second error by fitting the expectation value of $\langle H \rangle$ as a function of the standard deviation per configuration. Because the standard deviation per configuration is zero when $\langle H \rangle$ is exact, when we extrapolate our fit to zero this yields an estimate of the eigenvalue of the differential equation. Using a linear fit, this method produced an estimate for the relativistic energy for H_2^+ of -1.102471

± 0.000065 and -9498 ± 1 for Th_2^{179+} . The error on both of these estimates is large because of the small number of data points being used to determine the two constants in the linear fit. A larger number of basis functions would alleviate this problem but with our current wave-function form it is difficult to add additional functions because of the presence of numerous local minima. As an alternative we optimized the same size wave functions using three different random number sets. These were then expanded over the same set to give independent estimates of the relativistic energy. When these values were fitted (see Figs. 3 and 4), the improved estimates were determined to be -1.102565 ± 0.000011 for H_2^+ and -9498.97 ± 0.32 for Th_2^{179+} .

APPENDIX B. (NON)VARIATIONAL NATURE OF THE ENERGY

To understand the behavior of the variance, it is worthwhile to look at the individual terms in Eq. (5). When $u_2 = 0$ in Eq. (3), the expression for the small component u_3 is given by

$$Eu_3 = [V - c^2]u_3 - ic \frac{d}{dz} u_1 \quad (\text{B1})$$

whose solution can be found by minimizing the sum

$$\delta_3 = \sum_i \frac{u_3^2(\mathbf{x}_i)}{w(\mathbf{x}_i)^2} \left| [E - V + c^2]u_3(\mathbf{x}_i) + ic \frac{d}{dz} u_1(\mathbf{x}_i) \right|^2. \quad (\text{B2})$$

As the number of configurations goes to infinity, this expression is equivalent to

$$\delta_3 = \int \frac{u_3^2}{w} \left| [E - V + c^2]u_3 + ic \frac{d}{dz} u_1 \right|^2 d\tau. \quad (\text{B3})$$

Similar terms can be generated for δ_1 and δ_4 . Because the term $E = c^2$ dominates this integral, the numerator of Eq. (5) can be simplified to

$$\delta_3 \approx \int \frac{u_3^2}{w} \left| c^2 u_3 + c^2 u_3 - ic \frac{d}{dz} u_1 \right|^2 d\tau \quad (\text{B4})$$

or

$$u_3 = \frac{-i}{2c} \frac{d}{dz} u_1 + \frac{\varepsilon}{2c}, \quad (\text{B5})$$

where ε is a small quantity which represents all other terms. When the size of the small components

$$\delta_{\text{small}} = \int \frac{\varepsilon^2}{4w} |\nabla u_1|^2 d\tau \quad (\text{B6})$$

is compared to that of the large component

$$\delta_{\text{large}} = \int \frac{u_1^2}{w} \left| [E - V - c^2]u_1 + ic \frac{d}{dz} u_3 - ic \frac{d}{dx} u_4 + ic \frac{d}{dy} u_4 \right|^2 d\tau \quad (\text{B7})$$

$$\approx \int \frac{\varepsilon^2}{4w} |\nabla u_1|^2 d\tau, \quad (\text{B8})$$

we see that the small components depend on ∇u_1 in the same way that the large component depends on u_4 . In the event that we have an imperfect solution, the value of ε will cause u_1 or ∇u_1 to be as small as possible. The solution $u_1 = \nabla u_1 = 0$ is ruled out by the denominator in Eq. (5) but the

solutions $u_1 = 0, u_3 \approx \nabla u_1 > 0$ and $u_1 > 0, u_3 = 0$ are not. This means that large values of σ^2 can generate anomalous solutions. To find values of σ^2 less than the variance in the potential energy, there must be a cancellation of the r^{-1} singularity in the potential coming from the gradient of the small components in δ_1 . This is possible only for nonzero values of the small components, thus once σ^2 drops below this value the anomalous solution is no longer a problem.

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- [1] R. L. Coldwell, *Int. J. Quantum Chem.* **S11**, 215 (1977).
 [2] R. L. Coldwell and R. E. Lowther, *Int. J. Quantum Chem.* **S12**, 329 (1978).
 [3] R. L. Coldwell, *Int. J. Quantum Chem.* **S13**, 705 (1979).
 [4] R. E. Lowther and R. L. Coldwell, *Phys. Rev. A* **22**, 14 (1980).
 [5] S. A. Alexander, R. L. Coldwell, H. J. Monkhorst, and J. D. Morgan III, *J. Chem. Phys.* **95**, 6622 (1991).
 [6] S. A. Alexander, R. L. Coldwell, G. Aissing, and A. J. Thakkar, *Int. J. Quantum Chem.* **S26**, 213 (1992).
 [7] S. A. Alexander, R. L. Coldwell, and J. D. Morgan III, *J. Chem. Phys.* **97**, 8407 (1992).
 [8] S. A. Alexander and R. L. Coldwell, *Int. J. Quantum Chem.* **63**, 1001 (1997).
 [9] S. A. Alexander and R. L. Coldwell, *J. Chem. Phys.* **103**, 2572 (1995).
 [10] G. Aissing, *Phys. Rev. A* **44**, R2765 (1991).
 [11] F. Mark, L. Lischka, and F. Rosicky, *Chem. Phys. Lett.* **71**, 507 (1980).
 [12] L. Yang, D. Heinemann, and D. Kolb, *Chem. Phys. Lett.* **178**, 213 (1991).
 [13] L. LaJohn and J. D. Talman, *Chem. Phys. Lett.* **189**, 383 (1992).
 [14] R. Franke and W. Kutzelnigg, *Chem. Phys. Lett.* **199**, 561 (1992).
 [15] D. Sundholm, *Chem. Phys. Lett.* **223**, 469 (1994).
 [16] F. A. Parpia and A. K. Mohanty, *Chem. Phys. Lett.* **238**, 209 (1995).
 [17] R. Franke, *Chem. Phys. Lett.* **264**, 495 (1997).
 [18] L. LaJohn and J. D. Talman, *Theor. Chim. Acta* **99**, 351 (1998).
 [19] Y. Ishikawa, W. Rodriguez, and S. Torres, *Chem. Phys. Lett.* **143**, 289 (1988).
 [20] L. Laaksonen and I. P. Grant, *Chem. Phys. Lett.* **109**, 485 (1984).
 [21] H. A. Bethe and E. E. Salpeter, *The Quantum Mechanics of One and Two-Electron Atoms* (Plenum, New York, 1977), Sec. 14.
 [22] I. P. Grant and H. M. Quiney, *Adv. Quantum Chem.* **23**, 37 (1988).
 [23] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944), Sec. 11b.