# On the Use of Integral Electron Cusp Conditions as Constraints

C. P. YUE and D. P. CHONG

Department of Chemistry, University of British Columbia, Vancouver 8, B. C., Canada

Eleven approximate configuration-interaction wavefunctions for the ground state of helium are used to test the application of the integral electron cusp condition as a constraint. Our results indicate that, if the approximate wavefunction is flexible enough, the calculated electron density at the nucleus is improved when the cusp constraint is imposed. However, the expectation values of $r^{-2}$ and $r^{-1}$ do not change significantly.

Um die Anwendung der integralen Bedingung für den Elektronen-cusp zu überprüfen, wurden zur Berechnung des Heliumgrundzustandes elf approximierte CI-Wellenfunktionen benutzt. Die Resultate zeigen, daß bei genügend flexibler Wellenfunktion die berechnete Elektronendichte am Ort des Kerns verbessert wird, wenn man dem System die cusp-Bedingung auferlegt. Die Erwartungswerte für $r^{-2}$ und $r^{-1}$ ändern sich jedoch nur unbedeutend.

L'état fondamental d'Hélium était calculé avec once fonctions d'onde IC approximatives en vue d'examiner l'application de la condition intégrale de cusp électronique comme constraint. Les resultats montrent que avec cette constraint la densité électronique calculée au noyau est améliorée quand les fonctions d'onde sont assez flexible. Mais les valeurs expectatives pour $r^{-2}$ et $r^{-1}$ se ne changent pas drastiques.

## 1. Introduction

In a recent paper [1], Chong derived a set of integral coalescence conditions for exact wavefunctions. For approximate wavefunctions, the electron and spin coalescence values were defined, and the use of the coalescence conditions as constraints was proposed.

Let us consider the singlet ground state of an atom. For the exact wavefunction, one has an electron cusp condition:

$$\langle \Psi | \mathscr{G} | \Psi \rangle = \gamma \langle \Psi | \mathscr{Q} | \Psi \rangle , \qquad (1.1)$$

where

$$\mathscr{G} = \Sigma (4\pi r_i^2)^{-1} \delta(r_i) (\partial/\partial r_i) , \qquad (1.2)$$

$$\mathscr{Q} = \Sigma (4\pi r_i^2)^{-1} \delta(r_i) , \qquad (1.3)$$

$\gamma = -Z$, and $Z$ is the atomic number. For approximate wavefunctions, we define the electron cusp value $\Gamma$ and electron density at the nucleus $\Delta$ by:

$$\Gamma = \langle \Psi | \mathscr{G} | \Psi \rangle / \langle \Psi | \mathscr{Q} | \Psi \rangle , \qquad (1.4)$$

$$\Delta = \langle \Psi | \mathscr{Q} | \Psi \rangle / \langle \Psi | \Psi \rangle . \qquad (1.5)$$

Comparison of $\Gamma$ with $\gamma$ shows how well Eq. (1.1) is satisfied by an approximate wavefunction. On the other hand, it was proposed [1] that a better value for $\Delta$ may be obtained if the approximate wavefunction is constrained to satisfy Eq. (1.1). A simple constraint operator is:

$$\mathscr{C} = \tfrac{1}{2}(\mathscr{P} + \mathscr{P}^\dagger) , \qquad (1.6)$$

where                                      $\mathscr{P} = \mathscr{G} - \gamma \mathscr{Q}$.                          (1.7)

If an approximate wavefunction $\Psi$ satisfies

$$C = 0,$$                          (1.8)

where                                      $C = \langle \Psi | \mathscr{C} | \Psi \rangle$,                          (1.9)

then Eq. (1.1) is satisfied by $\Psi$, and $\Gamma = \gamma$.

In this work, we study the application of the constraint in Eq. (1.8) by testing it on eleven approximate configuration-interaction wavefunctions for the ground state of helium. Since the satisfaction of the cusp condition may improve other properties which are sensitive to $\Psi$ near the nucleus, the expectation values of $r^{-2}$ and $r^{-1}$ (besides $\Delta$) are also examined.

## 2. Calculations and Results

### Free Variation

The eleven approximate wavefunctions used in the present investigation are summarized in Table 1, the numeral subscript of each function signifying the number of configurations in that function. The orbital exponents, with the exception of $\phi_6$, have been crudely optimized; the coefficients for the terms in each function are calculated by the usual variational method.

Table 1. *Configurations and orbital exponents used. Each configuration (coefficient omitted) represents a* $^1S$ *function. The orbital exponents refer to the Slater-type orbitals in the order they appear*

| Function | Configurations | Orbital exponents |
|---|---|---|
| $\phi_3$ | $1s^2 + 1s2s + 2s^2$ | 2.348144,  1.661883 |
| $\phi_4$ | $1s^2 + 1s2s + 2s^2 + 2p^2$ | 2.251372,  1.627170,  2.479727 |
| $\phi_6$[a] | $1s^2 + 1s2s + 2s^2 + 1s3s$ $+ 2s3s + 3s^2$ | 1.908,  1.908,  1.908 |
| $\phi_7$[b] | $1s^2 + 1s2s + 2s^2 + 1s3s$ $+ 2s3s + 3s^2 + 2p^2$ | 1.575,  1.843,  1.955,  2.475 |
| $\psi_3$ | $1s1s' + 2s^2 + 2p^2$ | 2.160322,  1.238738,  4.088269, 2.472929 |
| $\psi_4$ | $1s1s' + 2s^2 + 2s3s + 3s^2$ | 1.739808,  1.354694,  3.365817, 2.486403 |
| $\psi_5$[b] | $1s1s' + 2s^2 + 2s3s + 3s^2 + 2p^2$ | 2.17621,  1.20152,  5.1,  5.1, 2.47547 |
| $\psi_7$ | $1s1s' + 2s^2 + 2s3s + 3s^2$ $+ 2s4s + 3s4s + 4s^2$ | 1.929838,  1.310046,  3.380943 2.532473,  2.880894 |
| $\psi_8$ | $1s1s' + 2s^2 + 2s3s + 3s^2$ $+ 2s4s + 3s4s + 4s^2 + 2p^2$ | 1.887365,  1.333773,  3.3601 2.611557,  3.013778,  2.475619 |
| $\varphi_3$ | $1s1s' + 1s''1s''' + 1s^{iv}1s^v$ | 1.148244,  2.417804,  1.360331, 1.646279,  1.8741,  4.1535 |
| $\varphi_4$ | $1s1s' + 1s''1s''' + 1s^{iv}1s^v + 2p^2$ | 1.140704,  2.503618,  1.3596, 1.726027,  1.8741,  4.1535,  2.469553 |

[a] Taken from H. Shull and P. O. Löwdin: J. chem. Physics **30**, 617 (1959).

[b] Taken from D. P. Chong and M. L. Benston: J. chem. Physics **49**, 1302 (1968).

Table 2. *Results of free variation (in atomic units). The percent derivation of $\Delta$ from the exact value is given in parentheses*

| Function | $E^a$ | $\Gamma^b$ | $\Delta^c$ | |
|---|---|---|---|---|
| $\varphi_3$ | $-2.876129$ | $-1.97625$ | $3.59342$ | $(-0.758)$ |
| $\phi_3$ | $-2.877406$ | $-1.99274$ | $3.61341$ | $(-0.206)$ |
| $\psi_4$ | $-2.877864$ | $-2.07110$ | $3.69098$ | $(+1.937)$ |
| $\phi_6$ | $-2.878296$ | $-2.00253$ | $3.63099$ | $(+0.280)$ |
| $\psi_7$ | $-2.878371$ | $-2.01147$ | $3.65662$ | $(+0.988)$ |
| $\varphi_4$ | $-2.895655$ | $-1.96899$ | $3.57623$ | $(-1.231)$ |
| $\psi_3$ | $-2.896548$ | $-2.12161$ | $3.68579$ | $(+1.793)$ |
| $\phi_4$ | $-2.896686$ | $-1.94580$ | $3.52533$ | $(-2.638)$ |
| $\psi_5$ | $-2.897142$ | $-1.95168$ | $3.61539$ | $(-0.151)$ |
| $\psi_8$ | $-2.897696$ | $-2.01225$ | $3.63465$ | $(+0.381)$ |
| $\phi_7$ | $-2.897840$ | $-1.98980$ | $3.60150$ | $(-0.535)$ |
| Exact | $-2.903724^d$ | $-2$ | $3.62085^d$ | $(0)$ |

[a] Energy.
[b] Cusp value at the nucleus.
[c] Electron density at the nucleus.
[d] Ref. [2].

Table 2, the results of free-variational calculations are presented. The entries are arranged in the order of decreasing energy $E$. The exact values for $E$ and $\Delta$ obtained by Pekeris [2] are included in the table for comparison.

## Constrained Variation

It should be noted that the operator $\mathscr{P}$ in Eq. (1.7) is not hermitian. The constraint operator $\mathscr{C}$, on the other hand, is hermitian by definition.

The two methods of solving constrained secular equations, namely, perturbation [3] and parametrization [4], have been well developed. Used in conjunction, the perturbation approach gives a value for the Lagrangian multiplier $\lambda$, which becomes an initial guess for the parameter in the parametrization approach. In practice, we find that, with the exception of $\phi_4$, the value of $\lambda$ from perturbation is so good that further parametrization becomes unnecessary.

The rapid rate of convergence of the perturbation series[1] is demonstrated by the following example of $\phi_7$:

$$\begin{aligned}
\lambda = &+1.031756 \times 10^{-3} - 1.06279 \times 10^{-5} \\
&+1.1119 \times 10^{-7} - 1.099 \times 10^{-9} \\
&+9.41 \times 10^{-12} - 6.07 \times 10^{-14} + \cdots \\
= &+1.021239 \times 10^{-3},
\end{aligned} \tag{2.1}$$

$$\begin{aligned}
\Delta E = &\,3.749950 \times 10^{-5} - 1.855863 \times 10^{-5} \\
&-1.26147 \times 10^{-7} - 9.4319 \times 10^{-10} \\
&-6.7909 \times 10^{-12} - 4.699 \times 10^{-14} \\
&-3.109 \times 10^{-16} + \cdots \\
= &\,1.881378 \times 10^{-5}.
\end{aligned} \tag{2.2}$$

[1] See Eqs. (19) and (22) of Ref. [4].

When the value of $1.021239 \times 10^{-3}$ is used for $\lambda$ in the parametrization method, the cusp constraint is satisfied to within $0.5 \times 10^{-7}$.

The results of constrained-variational calculations on the eleven approximate wavefunctions are summarized in Table 3. The quantity $\Delta E$ is the sacrifice in energy when the cusp constraint is imposed; it can be seen to be insignificant. The last column $\Delta$ is the electron density at the nucleus, calculated with the constrained wavefunction (see Discussion).

Table 3. *Results of constrained variation (in atomic units). The percent deviation of $\Delta$ from the exact value is given in parentheses*

| Function | $10^3 \lambda$ | $10^5 \Delta E$[a] | $\Delta$[b] | |
|---|---|---|---|---|
| $\varphi_3$ | $+\ 1.392867$ | 6.01 | 3.64996 | $(+0.804)$ |
| $\phi_3$ | $+\ 6.209249$ | 8.20 | 3.66617 | $(+1.252)$ |
| $\psi_4$ | $-\ 1.837415$ | 23.76 | 3.58552 | $(-0.976)$ |
| $\phi_6$ | $-\ 0.2876273$ | 0.13 | 3.62446 | $(+0.100)$ |
| $\psi_7$ | $-\ 0.0846074$ | 0.18 | 3.64547 | $(+0.680)$ |
| $\varphi_4$ | $+\ 1.494586$ | 8.28 | 3.54972 | $(-1.964)$ |
| $\psi_3$ | $-\ 2.270682$ | 50.18 | 3.58426 | $(-1.010)$ |
| $\phi_4$ | $+55.6501$ | 562.5 | 3.94843 | $(+9.047)$ |
| $\psi_5$ | $+\ 0.5008557$ | 4.38 | 3.62460 | $(+0.104)$ |
| $\psi_8$ | $-\ 0.07278035$ | 0.16 | 3.62387 | $(+0.083)$ |
| $\phi_7$ | $+\ 1.021239$ | 1.88 | 3.62639 | $(+0.153)$ |

[a] $\Delta E$ is the sacrifice in energy.
[b] See footnote c, Table 2.

## 3. Discussion

Using twenty-five approximate wavefunctions (available in the literature) for the ground state of helium, Chong and Schrader [5] recently showed that there exists a strong statistical correlation between the accuracies of $\Gamma$ and $\Delta$. As can be seen from Table 2, our present free-variational results confirm their finding qualitatively. Our results also indicate that an approximate wavefunction with a better energy does not necessarily give a better $\Gamma$ or $\Delta$, again in agreement with Chong and Schrader.

In general, we find that the application of the cusp constraint has a tendency to overcorrect the deviation of $\Delta$ from the exact value. When the approximate function is not flexible enough, the value of $\Delta$ from the constrained wavefunction may even be worse than that from the free-variational function. The case of $\phi_7$ is a typical example of this overcorrection. Table 4 shows the behavior of various quantities as the parameter $\lambda$ is varied in this case. However, the functions with more than four terms indicate that when the approximate wavefunction is flexible enough, the calculated value of $\Delta$ improves as one imposes the cusp constraint. Our best result appears in the case of $\psi_8$ which is also the most flexible function of the eleven.

As mentioned in the Introduction, the satisfaction of the cusp condition is expected to improve other properties which depend strongly on the wavefunction near the nucleus. For this reason, we examine the expectation values of $r^{-2}$ and $r^{-1}$ for some of our more flexible wavefunctions. The expectation value of $r^{-1}$

Table 4. *Typical behavior of various quantities as a function of* $\lambda$ *( as illustrated in the case of* $\phi_7$ *). The percent deviation of* $\Delta$ *from the exact value is given in parentheses*

| $10^3 \lambda$ | $10^5 \Delta E$ [a] | $10^2 C$ [b] | $\Gamma$ [c] | $\Delta$ [d] | |
|---|---|---|---|---|---|
| 0 | 0 | 3.672 | 1.98980 | 3.60150 | $(-0.535)$ |
| 0.2 | 0.7 | 2.959 | 1.99180 | 3.60633 | $(-0.401)$ |
| 0.4 | 1.2 | 2.243 | 1.99379 | 3.61118 | $(-0.267)$ |
| 0.6 | 1.6 | 1.524 | 1.99579 | 3.61606 | $(-0.132)$ |
| 0.8 | 1.8 | 0.802 | 1.99778 | 3.62095 | $(+0.003)$ |
| 1.02124 | 1.9 | 0 | 2.00000 | 3.62639 | $(+0.153)$ |

[a] See footnote a, Table 3.
[b] $C$ indicates how well the constraint is satisfied, see Eq. (1.8)
[c] See footnote b, Table 2.
[d] See footnote c, Table 2.

Table 5. *Expectation values of* $r^{-2}$ *and* $r^{-1}$ *for the more flexible wavefunctions*

| Function | Free | | Constrained | |
|---|---|---|---|---|
| | $\langle r^{-2} \rangle$ | $\langle r^{-1} \rangle$ | $\langle r^{-2} \rangle$ | $\langle r^{-1} \rangle$ |
| $\phi_6$ | 12.0404 | 3.37208 | 12.3031 | 3.37153 |
| $\psi_7$ | 12.1081 | 3.38438 | 12.0985 | 3.38389 |
| $\psi_8$ | 12.0744 | 3.38402 | 12.0659 | 3.38367 |
| $\phi_7$ | 12.0100 | 3.37354 | 12.0451 | 3.37547 |
| Exact [a] | 12.0341 | 3.37663 | 12.0341 | 3.37663 |

[a] Ref. [2].

is closely related to the diamagnetic contribution to the shielding constant $\sigma^d$. The results, listed in Table 5, are somewhat disappointing. These results suggest that, in order to improve the expectation values of $r^{-2}$ and $r^{-1}$, some other constraint must be used.

In short, we have learned from this study: (a) that the wavefunction must be flexible enough in order to take advantage of the cusp constraint; and (b) that the cusp constraint has little effects on the expectation values of $r^{-2}$ and $r^{-1}$; but (c) that the calculated value of $\Delta$ improves when one impose the cusp constraint on an approximate wavefunction with enough linear coefficients.

## References

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Dr. Delano P. Chong
Department of Chemistry
University of British Columbia
Vancouver 8, Canada