

## A comparison of $V_N$ and $V_{N-1}$ potential results in manybody calculations of spectroscopic parameters

S. Ahmad

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pure  $\text{CH}_4$  at a temperature consistent with a smooth extension of the lower phase line, suggesting that the result is a real, if transient, effect.

The existence of a region of metastable phase III raises two questions: (1) what causes the destabilization of the phase III structure, and (2) what are the ramifications of the termination of the II–III phase line? Neither question can be readily answered.

Extensive calculations using the EJK model have indicated that the stability of phase III in  $\text{CH}_4$  depends critically on the relative populations of the coupled nuclear spin–rotation states.<sup>11</sup> If transitions between these states occur (spin conversion), the net effect is to destabilize phase III, because the symmetric ground state is less sensitive to the orientational field. The phase III structure predicted by the theory is, however, incorrect,<sup>12</sup> and thus the theoretical prediction can be considered only to indicate a possible cause of the destabilization. Some simple arguments suggest that it is not the primary reason.

In phase II,  $\text{CH}_4$  spin conversion on the disordered sites is relatively rapid at temperatures above 8 K,<sup>13</sup> and so an increase in the ground state population is possible. In phase III, however, all of the sites are ordered and spin conversion is only energetically favored below 4 K.<sup>14</sup> Any sample that manages to enter phase III should have its spin species distribution frozen to correspond to some higher temperature composition. Clearly then, while the depopulation to the ground state may prevent phase III from forming, it should not be responsible for the destruction of phase III once it has formed. The stability of phase III thus seems to depend on very subtle changes in the intermolecular potential, so much so that a modest amount of  $\text{CD}_4$  can stabilize it.

As the amount of  $\text{CD}_4$  is decreased, the thermal data suggest that phase II and phase III are becoming more similar, until at about 15%  $\text{CD}_4$  equilibrium, phase III ceases to exist and phase II remains the stable phase down to much lower temperatures. This result would seem to indicate that phase III is closely related to phase II, but recent inelastic neutron scattering (INS) results suggest that there is little or no relationship between the two phases.<sup>1,15</sup> The source of this apparent disagreement is unclear.

On the basis of the present results alone, an alterna-

tive possibility cannot be ruled out. The disappearance of the enthalpy may not signal the destabilization of phase III, but rather that short range order in the two phases has become very similar. While that does not seem too likely, it will require a structure sensitive probe such as neutron diffraction to test it.

High resolution INS experiments and more precise calorimetry are planned in the near future to explore more fully the  $\text{CH}_4$ – $\text{CD}_4$  system in the region of metastability. Experiments will also be performed to check the role that spin conversion may play.

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## A comparison of $V^N$ and $V^{N-1}$ potential results in many-body calculations of spectroscopic parameters

S. Ahmad

*Department of Physics, State University of New York, Albany, New York 12222*  
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Discrete basis sets of one-electron wave functions in conjunction with linked cluster many-body perturbation theory have extensively been used in the past<sup>1</sup> to calculate several quantities pertaining to atomic properties in a variety of atoms and ions. This scheme is still in

active use and regarded to be successful in providing good results. In a recent many-body work,<sup>2</sup> employing a basis set based on  $V^N$ -type Hartree–Fock–Slater potential, it was reported that a particular diagram omitted in previous works<sup>3</sup> makes very large contribution to

the Sternheimer quadrupole antishielding parameter  $\gamma_\infty$ . On the basis of this investigation, the authors concluded that all the previous results employing  $V^{N-1}$  potential are considerably underestimated. Andriessen<sup>3</sup> made a comparative study of the equivalent contributions arising from this particular diagram, employing both  $V^N$  and  $V^{N-1}$  potential in  $\text{Gd}^{3+}$ . This work concluded that: (a) the particular contribution pointed out in Ref. 2 is indeed substantial; however, the quoted value is too large because of an error<sup>4</sup> in a multiplying factor depending upon the integrations over the angular part of the wave functions, and (b) because of the omission of this particular contribution in earlier works, the results thus far have been underestimated.

In view of the usefulness of such a comparison, it seemed desirable to make a comparative study of various contributions using different methods in a particular system. In this communication, we report the results of such a study in beryllium atom. We chose the Be atom because this presents a very simple system, and results for this atom based on various methods are available in the literature.

Results of the present calculation using linked cluster many-body perturbation theory, employing a procedure discussed elsewhere,<sup>5</sup> are presented in Table I. This table also includes for comparison some other results available in the literature. A comparison of the first three sets of values, which correspond to three different methods, shows that the results are in good general agreement. On the other hand, the last entry in this table indicates that the results provided by the Sternheimer<sup>6</sup> procedure are considerably different from others.

Higher-order contributions are presented in Table II. Because of the nonavailability of higher order contributions based on the  $V^N$  potential, we present, for comparison, similar results by Kelly<sup>10</sup> using the  $V^{N-1}$  potential; therefore the comparison of the two results is meaningful only in their totals when they are summed to higher orders. Our result corresponds up to third order only; the obtained agreement is quite satisfying. As the experimental determinations of these quantities are quite uncertain, it is difficult to assess the reliability of these results in this respect. However,  $\beta_\infty$  for a neutral atom is known to be 1.0 by exact theory<sup>6</sup> and the comparison shows that the calculated  $\beta_\infty$  values for Be are close enough. Our value of 1.2 seems to be slightly larger.

TABLE I. Zero-order contributions to the electric dipole and quadrupole polarizabilities ( $\alpha_d$ ,  $\alpha_q$ ) and shielding factors ( $\beta_\infty$ ,  $\gamma_\infty$ ) in Be.

	$\alpha_d$ ( $\text{\AA}^3$ )	$\beta_\infty$	$\alpha_q$ ( $\text{\AA}^5$ )	$\gamma_\infty$
1s contribution	0.0065	0.4126	0.0006	0.0968
2s contribution	3.7954	1.0733	11.8135	0.7406
Total	3.802	1.486	11.814	0.837
Total <sup>a</sup>	4.54	1.77	9.26	0.67
Total <sup>b</sup>	4.5	1.8	9.1	0.77
Total <sup>c</sup>	9.5	4.4	15.1	1.24

<sup>a</sup>Using the  $V^N$  potential (Ref. 7).

<sup>b</sup>Using the uncoupled Hartree-Fock model (Ref. 8)

<sup>c</sup>Using the Sternheimer procedure (Ref. 9).

TABLE II.  $V^N$  and  $V^{N-1}$  contributions to the electric dipole and quadrupole polarizabilities ( $\alpha_d$ ,  $\alpha_q$ ) and shielding factors ( $\beta_\infty$ ,  $\gamma_\infty$ ) including higher orders.

Contribution	$\alpha_d$ ( $\text{\AA}^3$ )	$\beta_\infty$	$\alpha_q$ ( $\text{\AA}^5$ )	$\gamma_\infty$
Zero order <sup>a</sup>	3.802	1.486	11.814	0.837
First order <sup>a</sup>	1.653	-0.031	5.452	0.328
Second order <sup>a</sup>	-0.651	-0.250	-0.834	-0.084
Total <sup>a</sup>	4.80	1.20	16.43	1.08
Zero order <sup>b</sup>	12.15	4.30	15.1	1.06
Higher orders <sup>b</sup>	-5.22	-3.33	-1.0	-0.31
Total <sup>b</sup>	6.93	0.97	14.1	0.75

<sup>a</sup>Using the  $V^N$ -type potential (present work).

<sup>b</sup>Using the  $V^{N-1}$  potential (Ref. 10).

We presume that this is because of the neglect of higher order contributions beyond third order in our calculation.

This study demonstrates that if contributions from all valid diagrams are included, the calculated physical quantities using  $V^N$ - and  $V^{N-1}$ -type potentials in conjunction with many-body theory would agree with each other reasonably well, as, in principle, one would expect. However, results of  $\gamma_\infty$  values in  $\text{Na}^+$  employing the  $V^{N-1}$  potential<sup>11</sup> were found to be appreciably smaller than that obtained by employing the  $V^N$ -type potential.<sup>12</sup> After a revision of the former calculation,<sup>13</sup> this discrepancy was found to be arising because of the omission of a particular diagram, as we have mentioned earlier. This therefore suggests that  $\gamma_\infty$  results for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  employing the  $V^{N-1}$  potential<sup>14,15</sup> are also underestimated and probably need a revision.

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