

## Effective Magnetic Field and Gradient of Electric Field Acting on the Nucleus of Eu in Europium Iron Garnet\*

G. GILAT AND I. NOWIK

*Department of Physics, The Hebrew University, Jerusalem, Israel*

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The internal effective magnetic field ( $H_{\text{eff}}$ ) and the electric field gradient acting on europium nuclei in europium iron garnet has been calculated. The nondiagonal matrix elements connected with the admixture of states produced by the exchange interaction give the main contribution to these fields. The temperature dependence of these fields is compared with the dependence of the magnetic moment of the ion as calculated by Wolf and Van Vleck. The effective magnetic field at 0°K turns out to be  $7 \times 10^6$ Oe, whereas, the electric field gradient at 0°K is  $eq/h = -555$  Mc/sec per b. In an Appendix the paramagnetic correction for the internal magnetic field acting on the nucleus of Eu in the presence of an external magnetic field is also calculated as a function of temperature. At room temperature  $H_{\text{int}} = 1.54 H_0$ .

### INTRODUCTION

IN some recent researches,<sup>1-3</sup> using the Mössbauer effect and  $\gamma$ - $\gamma$  angular correlations in rare-earth iron garnets, effective magnetic fields, acting on the rare-earth nuclei, have been observed. This effective field is to be associated with the hyperfine interaction which is orientated as a consequence of the exchange interaction existing between the iron and the rare-earth sublattices in the garnet, below the Curie temperature. This exchange interaction also gives rise to the spontaneous magnetization of the rare-earth sublattice in the iron garnet.<sup>4</sup> Neglecting the effect of crystalline fields, i.e., assuming "free" rare-earth ions which are acted on only by the exchange field and taking into account the ionic ground state alone, the magnetization and the effective magnetic field ( $H_{\text{eff}}$ ) should be similarly dependent on temperature, since both depend in the same way on the Boltzmann average of  $J_z$  (where  $J_z$  is the projection of  $J$  in the direction of the exchange field). Recent measurement<sup>1</sup> seems to confirm the proportionality between the magnetization and  $H_{\text{eff}}$  for Dy in dysprosium iron garnet (DIG), justifying in this case, at least, the free-ion approximation.

As was pointed out by Wolf and Van Vleck<sup>5</sup> the situation in the case of EuIG is quite different. The ionic ground state for  $\text{Eu}^{3+}$  is  ${}^7F_0$ , which is diamagnetic. On the other hand, there is an appreciable exchange interaction acting on the spin of this ion in the garnet. Moreover, there exist excited ionic levels, namely,  ${}^7F_1$  and  ${}^7F_2$ , at energies which are relatively low and, therefore, are introduced as admixtures in the ground state, when taking into account the exchange interaction. This perturbed ground state gives rise to a nonzero spontaneous magnetization, as well as to a nonzero effective magnetic field. In addition, there is a

direct contribution of these excited levels (especially  ${}^7F_1$ ) owing to its thermal population as a function of temperature. Wolf and Van Vleck,<sup>5</sup> using this approach, gave a satisfactory explanation to the spontaneous magnetization of EuIG as a function of temperature. They pointed out that the free-ion approach is justifiable for the case of EuIG since the point symmetry at the  $\text{Eu}^{3+}$  site is almost cubic, and a cubic field cannot remove the degeneracy for  $J < 2$ .

We use, essentially, the same idea in this work in order to calculate the internal effective magnetic field acting on the Eu nucleus in EuIG as a function of temperature. A similar procedure for calculating  $H_{\text{eff}}$  when influenced by an excited ionic level has been used by Caspari, Frankel, and Wood<sup>2</sup> in the case of  $\text{Sm}^{3+}$  in samarium iron garnet, where the energy of the excited state is again relatively low. This approach, however, has not been successful in calculating the spontaneous magnetization in<sup>6</sup> SmIG and as yet there is no satisfactory explanation of the behavior of the magnetization as a function of temperature.

In addition, we have also used the free-ion approach in order to calculate the electric field gradient produced by the orbitals of the  $4f$  electron shell which, in general, will be partially aligned under the influence of the exchange interaction and therefore correlated with the magnetization, as was pointed out by Bauminger *et al.*<sup>1</sup> This electric field gradient is perhaps the most significant one in the case of  $\text{Eu}^{3+}$  in EuIG.

There is some interest in calculating these two quantities since recently it has been shown that one can carry out Mössbauer experiments in EuIG, using the isotope  $\text{Eu}^{151}$  which has a first excited state of 22 keV and gives large recoil-free effects.<sup>7</sup> Since one can achieve an emission line of almost natural linewidth<sup>7,8</sup> and there is a possibility to perform the

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<sup>1</sup> R. Bauminger, S. G. Cohen, A. Marinov, and S. Ofer, *Phys. Rev. Letters* **6**, 467 (1961).

<sup>2</sup> M. E. Caspari, S. Frankel, and G. T. Wood, *Phys. Rev.* **127**, 1519 (1962).

<sup>3</sup> S. G. Cohen and G. Gilat, *Nucl. Phys.* **38**, 1 (1962).

<sup>4</sup> R. Pauthenet, *Ann. Phys. (N. Y.)* **3**, 424 (1958).

<sup>5</sup> W. P. Wolf and J. H. Van Vleck, *Phys. Rev.* **118**, 1490 (1960).

<sup>6</sup> J. A. White and J. H. Van Vleck, *Phys. Rev. Letters* **6**, 412 (1961).

<sup>7</sup> D. A. Shirley, M. Kaplan, R. W. Grant, and D. A. Keller, *Phys. Rev.* **127**, 2097 (1962).

<sup>8</sup> The mean lifetime of the first excited state in  $\text{Eu}^{151}$  (22 keV;  $+7/2$ ) was measured in our laboratory by I. Nowik and S. Ofer using conventional coincidence technique and was found to be  $\tau < 10.5 \times 10^{-9}$  (unpublished).

experiment in a large range of temperatures, one should be able to study experimentally the behavior of the effective magnetic field and perhaps also the electric field gradient acting on the nucleus as a function of temperature.

In an Appendix the paramagnetic correction for the internal magnetic field acting on the nucleus of Eu in the presence of an external magnetic field is also calculated.

### THEORY

As was mentioned above, we make use here of the free ion approximation. We start with the Hamiltonian<sup>5</sup>

$$\mathcal{H} = A(\mathbf{L} \cdot \mathbf{S}) + 2\beta_0(\mathbf{H}_{\text{exch}} \cdot \mathbf{S}), \quad (1)$$

where we do not introduce an external field. Using first-order perturbation theory we calculate the admixed eigenstates for  $J=0; 1; 2; 3$ . The energies for the excited ionic levels  ${}^7F_1$ ,  ${}^7F_2$ , and  ${}^7F_3$  are taken to be<sup>9</sup> 480°K, 1330°K, and 2600°K. The effective field acting on the nucleus is calculated using the hyperfine interaction operator<sup>10</sup>

$$N = \sum_i \left( \mathbf{1}_i - \mathbf{s}_i + \frac{3(\mathbf{s}_i \cdot \mathbf{r}_i)\mathbf{r}_i}{r_i^2} \right). \quad (2)$$

The internal effective field is proportional to the average component of the hyperfine interaction operator along the direction of the exchange interaction, which we denote by the  $Z$  axis. We first express the matrix elements of  $N$  in the perturbed scheme and then perform its thermal average with respect to the ionic

levels concerned. This is represented by  $\langle N_z \rangle_T$ ; then  $H_{\text{eff}}$  is given by

$$H_{\text{eff}} = 2\beta_0 \langle r^{-3} \rangle \langle N_z \rangle_T. \quad (3)$$

The operator equivalents of  $N$  in the ( $JLS$ ) scheme are calculated from the work of Elliott and Stevens.<sup>11</sup> In our calculation we take into account also the contributions from the thermal population of the ionic levels  ${}^7F_1$  and  ${}^7F_2$  (the energies of which are denoted by  $E_1$  and  $E_2$ , respectively). We then obtain for  $H_{\text{eff}}$

$$H_{\text{eff}} = 2\beta_0^2 \langle r^{-3} \rangle H_{\text{exch}}(T) (1 + 3e^{-E_1/kT} + 5e^{-E_2/kT})^{-1} \\ \times \left[ \frac{40}{3E_1} + e^{-E_1/kT} \left( -\frac{40}{3E_1} + \frac{26}{E_2 - E_1} - \frac{2}{3kT} \right) \right. \\ \left. + e^{-E_2/kT} \left( -\frac{26}{E_2 - E_1} + \frac{332}{9(E_3 - E_2)} - \frac{32}{9kT} \right) \right]. \quad (4)$$

Since we are interested in comparing the temperature dependence of  $H_{\text{eff}}$  with the magnetization of the Eu sublattice in the EuIG, we have extended the calculation carried out by Wolf and Van Vleck up to the same order as that of  $H_{\text{eff}}$ . We obtain for the average magnetic moment

$$\mu = \beta_0^2 H_{\text{exch}}(T) (1 + 3e^{-E_1/kT} + 5e^{-E_2/kT})^{-1} \\ \times \left[ \frac{16}{E_1} + e^{-E_1/kT} \left( -\frac{16}{E_1} + \frac{30}{E_2 - E_1} + \frac{3}{kT} \right) \right. \\ \left. + e^{-E_2/kT} \left( -\frac{30}{E_2 - E_1} + \frac{40}{E_3 - E_2} + \frac{15}{kT} \right) \right]. \quad (5)$$

The temperature dependence of both curves is shown in Fig. 1 (assuming  $\langle 1/r^3 \rangle$  is  $57 \times 10^{24} \text{ cm}^3$ ).<sup>12</sup> The temperature dependence for  $H_{\text{exch}}$  is derived in the same way as was done in reference 5 using the value of  $\beta_0 H_{\text{exch}}^{(0)}/k = 24^\circ\text{K}$ .

In the case of the electric field gradient, the operator under consideration is given by

$$q_z = e \langle r^{-3} \rangle \sum_i (3 \cos^2 \theta_i - 1). \quad (6)$$

The electric field gradient is, essentially, calculated in the same manner, but here we have to consider a second-order admixture in the ionic eigenstates, since the first-order perturbation is zero. Elliott<sup>13</sup> has calculated in a similar way the quadrupole interaction for europium nuclei in axially symmetric crystalline fields arising from the admixture of  $F_2$  into  $F_0$  produced by the crystalline field interactions. For the thermal average of the matrix elements it is sufficient to consider the contribution of the first two states only.

The matrix elements of this operator in the ( $JLS$ )

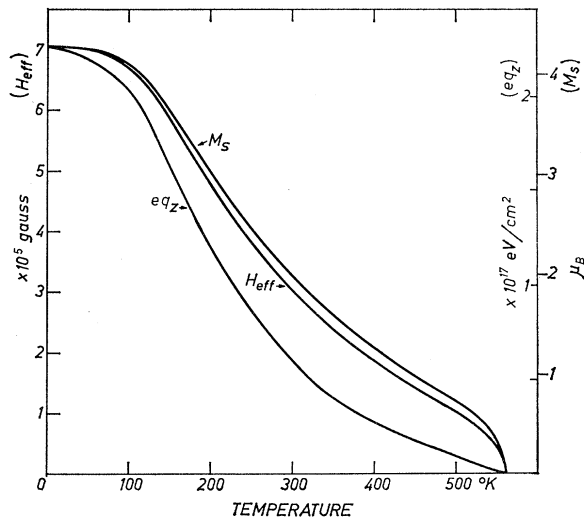


FIG. 1. The temperature dependence of the effective magnetic field and the electric field gradient acting on the nucleus of Eu in EuIG. For comparison the temperature dependence of the magnetic moment of the europium ion in EuIG is given.

<sup>9</sup> H. Gobrecht, Ann. Physik 28, 673 (1937); and also J. H. Van Vleck, Ann. Inst. Henri Poincaré 10, 80 (1947).

<sup>10</sup> A. Abragam and M. H. L. Pryce, Proc. Phys. Soc. (London) A205, 135 (1951).

<sup>11</sup> R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) 218, 553 (1953).

<sup>12</sup> B. Bleaney, Proc. Phys. Soc. (London) A68, 937 (1955).

<sup>13</sup> R. J. Elliott, Proc. Phys. Soc. (London) B70, 119 (1957).

scheme are, apart from their sign, those of a single electron, since we have here a "hole" in a half-filled 4*f* shell. We use here Eq. (44) of Racah<sup>14</sup> for the evaluation of the matrix element of the tensor  $C_0$ .<sup>2</sup>

We obtain for the thermal average of  $q_z$

$$\langle q_z \rangle_T = e \langle r^{-3} \rangle \beta_0^3 H_{\text{exch}}^2(T) (1 + 3e^{-E_1/kT})^{-1} \times \left\{ \frac{32(2E_1 + E_2)}{5E_1^2 E_2} + e^{-E_1/kT} \left[ \frac{1}{-5k^2 T^2} + \frac{1}{5(E_2 - E_1)} \left( \frac{12}{kT} - \frac{64}{E_1} + \frac{22}{E_2 - E_1} + \frac{96}{E_3 - E_1} \right) \right] \right\}. \quad (7)$$

The temperature dependence of  $\langle q_z \rangle_T$  is also shown in Fig. 1. The expression for the quadrupole interaction energy is

$$E_Q = e \langle q_z \rangle_T Q [3I_z^2 - I(I+1)] / 4I(2I-1); \quad (8)$$

for  $Q(\text{Eu}^{151}) = 0.95 \text{ b}$ ,<sup>15</sup> a value of  $eqQ/h = -530 \text{ Mc/sec}$  at 0°K is obtained neglecting shielding effects.<sup>16</sup>

In addition to this, one should consider two other contributions to the quadrupole interactions: (a) that produced by the ionic Stark levels of  $\text{Eu}^{3+}$  in the presence of the crystalline field, and (b) that produced by the external distribution of ionic charges in the lattice which is magnified by a large antishielding factor  $\gamma_\infty = -70$ , according to recent calculations by Wikner and Burns.<sup>17</sup>

The case of europium ethylsulfate, the symmetry of which is lower than cubic, was extensively investigated, theoretically and experimentally. Contribution (a) was calculated by Elliott<sup>13</sup> and is about  $eqQ/h \sim +60 \text{ Mc/sec}$ . Contribution (b) was calculated from optical data<sup>17</sup> and is  $eqQ/h \sim -35 \text{ Mc/sec}$ . An experimental result of  $eqQ/h \sim -140 \text{ Mc/sec}$  was obtained by Judd *et al.*<sup>18</sup> It seems reasonable that these contributions [(a) and (b)] in EuIG are at most of the same magnitude as in europium ethylsulfate. Some support for this assumption is supplied by a calculation<sup>19</sup> for ytterbium gallium garnet, where the departure from cubic symmetry is estimated, and the relevant expression for calculating the ionic electric field gradient<sup>17</sup> is derived  $A_2^0 \approx 50 \text{ cm}^{-1}$ , which is less than that for the case of europium ethyl sulfate  $A_2^0 \approx 120 \text{ cm}^{-1}$ . All this suggests that for EuIG, the exchange interaction contribution to the quadrupole interaction is dominant.

$H_{\text{eff}}$  at 0°K is about  $7.10^5 \text{ Oe}$ , according to the above

calculations. For the ground state of  $\text{Eu}^{151}$  the magnetic moment is 3.6 nm and the magnetic Zeeman splitting  $g\mu_n H_{\text{eff}}/h$  will be of the order of 700 Mc/sec. Another contribution to  $H_{\text{eff}}$  which is generally neglected is the core polarization which was estimated roughly by Freeman and Watson<sup>20</sup> to be  $-9 \times 10^4 S \text{ Oe}$ , where  $S$  is the spin. In the case of  $\text{Eu}^{3+}$ , where the effective magnetic field is relatively small the contribution of core polarization must be considered. This contribution is negative and therefore diminishes the total effective magnetic field.

It is seen from Fig. 1 that these calculations predict that the temperature dependence of  $H_{\text{eff}}$  and the magnetization of the europium sublattice should be somewhat different. The decrease of  $H_{\text{eff}}$  with increasing temperatures is much less than that to be expected for other (and as found for<sup>1</sup> DIG and<sup>21</sup> TmIG) rare-earth garnets.

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#### APPENDIX

It was pointed out by Goldring and Sharenberg<sup>22</sup> that when measuring nuclear gyromagnetic ratio using an external magnetic field  $H_0$  acting on a system of paramagnetic ions, the field at the nucleus  $H_{\text{int}}$  is equal to  $H_0(1+\beta)$ , where  $\beta$  is an important correction which must be taken into account. The origin of this correction is the magnetic hyperfine interaction partially aligned under the influence of the applied field. Manning and Rogers<sup>23</sup> have calculated this correction for all rare-earth ions, but neglected the admixture of the excited ionic states in the ground state in the case of  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ .<sup>24</sup>

Kanamori and Sugimoto<sup>25</sup> have calculated the temperature dependence of this correction for  $\text{Sm}^{3+}$  by taking into account this contribution. In the case of  $\text{Eu}^{3+}$ , where the ground state is  ${}^7F_0$ , this correction can be calculated in a very similar way to that of  $H_{\text{eff}}$  in ferrimagnetic europium iron garnet. The only difference is that the perturbing Hamiltonian in the present case is  $\beta_0(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H}_0$ , where  $H_0$  is the external field, instead of  $2\beta_0(\mathbf{S} \cdot \mathbf{H}_{\text{exch}})$  in the ferrimagnetic case, since for the latter the exchange field ( $H_{\text{exch}}$ ) acts only on the spin.

<sup>20</sup> A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

<sup>21</sup> I. Nowik and S. Ofer, Phys. Letters **3**, 192 (1963).

<sup>22</sup> G. Goldring and R. P. Scharenberg, Phys. Rev. **110**, 701 (1958).

<sup>23</sup> G. Manning and J. Rogers, Nucl. Phys. **15**, 166 (1960).

<sup>24</sup> J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

<sup>25</sup> J. Kanamori and K. Sugimoto, J. Phys. Soc. (Japan) **13**, 754 (1958).

<sup>14</sup> G. Racah, Phys. Rev. **62**, 438 (1942).

<sup>15</sup> K. Krebs and R. Winkler, Naturwiss. **47**, 490 (1960).

<sup>16</sup> R. M. Sternheimer, Phys. Rev. **95**, 736 (1954).

<sup>17</sup> E. G. Wikner, G. Burns, Phys. Letters **2**, 225 (1962).

<sup>18</sup> B. R. Judd, C. A. Lovejoy, and D. A. Shirley, Phys. Rev. **128**, 1733 (1962).

<sup>19</sup> J. Thomas, Ph.D. thesis, University of Grenoble, France, 1962.

Calculation of  $\beta$  as a function of temperatures gives

$$\beta = \beta_0^2 \langle r^{-3} \rangle (1 + 3e^{-E_1/kT} + 5e^{-E_2/kT})^{-1} \\ \times \left[ \frac{40}{3E_1} + e^{-E_1/kT} \left( -\frac{40}{3E_1} + \frac{26}{E_2 - E_1} - \frac{2}{kT} \right) \right. \\ \left. + e^{-E_2/kT} \left( -\frac{26}{E_2 - E_1} + \frac{332}{9(E_3 - E_2)} - \frac{32}{3kT} \right) \right], \quad (\text{A1})$$

where all the related parameters are defined above in this article.

At 300°K for instance,  $\beta = 0.54$  (giving  $H_{\text{int}} = 1.54H_0$ ) instead of a value of  $\beta = 0$ , when the excited ionic levels are ignored. This relatively large correction would be important for the determination of nuclear gyromagnetic ratios of excited states of europium isotopes using angular correlation technique.

*Note added in proof.* Recent Mossbauer measurements carried out by I. Nowik and S. Ofer in this laboratory, and to be submitted for publication shortly, show that at 80°K  $H_{\text{eff}}$  is about 750 kOe, in very good agreement with the present calculations.

## Boltzmann Equation for Polarons\*

LEO P. KADANOFF

*Department of Physics, University of Illinois, Urbana, Illinois*

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The Feynman description of the polaron is used to write down a polaron Boltzmann equation. This equation is then used to discuss the drift mobility problem. In the limit of low temperatures, the Boltzmann equation is rearranged to exhibit elastic resonance scattering and it is solved exactly. The evaluation of the drift mobility thus obtained is compared with the results of other calculations. Other applications of the polaron Boltzmann equation are briefly discussed.

### INTRODUCTION

IN this paper, we calculate the drift mobility of an electron in a polar crystal (a polaron) by making use of a model due to Feynman.<sup>1-3</sup> Our procedure will be to use the Feynman model to derive a Boltzmann equation which may then be solved to find the mobility. Extensive study<sup>4-7</sup> has already been devoted to this mobility problem. The primary novel feature of the present work is the use of a Boltzmann equation in conjunction with the Feynman model.

We begin from the Fröhlich Hamiltonian for an electron in a polar crystal. We take all the optical phonons to have the same frequency and the electron-phonon matrix element to be proportional to the inverse of the magnitude of the phonon wave vector. In units in which  $\hbar$ , the phonon frequency, and the electron band mass are all equal to unity the Fröhlich Hamiltonian is<sup>8</sup>

$$H = \mathbf{p}_e^2/2 + U(\mathbf{r}_e, t) + \sum_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \\ + \sum_{\mathbf{q}} \left( \frac{4\pi\alpha}{\sqrt{2}Vq^2} \right)^{1/2} (a_{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}_e} + a_{\mathbf{q}}^\dagger e^{-i\mathbf{q} \cdot \mathbf{r}_e}). \quad (1)$$

\* Supported in part by the U. S. Army Research Office (Durham).

<sup>1</sup> R. P. Feynman, Phys. Rev. **97**, 660 (1955).

<sup>2</sup> Y. Osaka, Progr. Theoret. Phys. (Kyoto) **22**, 437 (1959).

<sup>3</sup> T. D. Schultz, Phys. Rev. **116**, 526 (1959).

<sup>4</sup> D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

<sup>5</sup> F. E. Low and D. Pines, Phys. Rev. **98**, 414 (1958).

<sup>6</sup> Y. Osaka, Progr. Theoret. Phys. (Kyoto) **25**, 517 (1961).

<sup>7</sup> R. P. Feynman, R. W. Hellwarth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962), denoted as FHIP.

<sup>8</sup> H. Fröhlich, Advan. Phys. **3**, 325 (1954).

Here,  $\mathbf{p}_e$  and  $\mathbf{r}_e$  are electron momentum and position operators;  $a_{\mathbf{q}}^\dagger$  and  $a_{\mathbf{q}}$  are operators which create and destroy a phonon with wave vector  $\mathbf{q}$ ;  $V$  is the volume of the system;  $\alpha$  is a dimensionless coupling constant which measures the strength of the electron-phonon interaction.  $U(\mathbf{r}, t)$  is a scalar potential for a force externally applied to the system. At the space-time point  $\mathbf{r}, t$ , this force is, of course,  $-\nabla U(\mathbf{r}, t)$ . We shall use this force to set the polaron in motion so that we may measure its mobility.

In the weak coupling limit,  $\alpha \ll 1$ , we can apply a perturbation expansion in the electron-phonon interaction. We can take the basic electronic states to be plane wave states and write a Boltzmann equation to describe how phonon emission and absorption processes change the population of these states.<sup>4</sup> However, when  $\alpha$  is comparable with or greater than unity this description of the electronic states breaks down. Every electron now travels with a cloud of phonons about it and this cloud substantially modifies all the electronic properties.

However, there exists a relatively simple description of the polaron which works quite well even when  $\alpha$  is fairly large. Feynman<sup>1</sup> pointed out that the motion of the electron in its associated cloud of phonons was quite similar to the motion that an electron would go through if it were coupled to another particle<sup>5</sup> with a harmonic oscillator coupling. If this fictitious other particle has mass  $M$  and the spring constant is  $k$ , then the Hamiltonian for this analog system is

$$H_0 = \mathbf{p}_e^2/2 + \mathbf{P}^2/2M + \frac{1}{2}k(\mathbf{r}_e - \mathbf{R})^2. \quad (2)$$